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# THE ATOMIC AND MOLECULAR FORCES OF CHEMICAL AND PHYSICAL INTERACTION IN LIQUIDS AND GASES, AND THEIR EFFECTS.

BY

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[Dedicated to my research student comrades of the past, in remembrance  
of the many pleasant and instructive hours spent together.]

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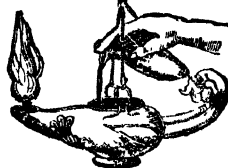
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## PREFACE.

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THIS book deals with the nature of the law of force between the atoms and molecules of liquids and gases, and its connexion with their physical and chemical properties. The subject has attracted some attention, and given rise to a good deal of speculation. Since the molecules in a liquid or gas undergo motions of translation and rotation, and probably undergo contractions and expansions under each other's varying influence, the nature of the law cannot yet be deduced from the electronic structure of the atoms and molecules. Since these rotations and contractions would take place in a way such as to render the potential energy of attraction a minimum, they would evidently very much influence the nature of the law of force between the molecules. Its nature can therefore be deduced only from the physical properties of liquids and gases as a whole.

The law that holds between the atoms of a solid, which we know do not undergo any appreciable motions of translation or rotation, or that between two stationary atoms, may therefore be of an entirely different character from that which would hold if the atoms formed part of a liquid or gas. The forces acting in the former case have already been investigated in connexion with the compressibility of solids, etc. In that case the atoms are so close to each other that the forces

between them are entirely governed by the electronic configuration of the atoms, and the way they face each other. This phase of the atomic forces will not be dealt with in this monograph.

The law of force between two molecules undergoing rotations in a liquid or gaseous substance most necessarily be complicated in character. It has to account for repulsion at close approach, for repulsion at considerable distances of separation, as shown by the Joule Thomson effect, and for attraction at distances in between. Its determination from the facts can therefore from the nature of things be only an approximation to the true law. The law as a whole can, however, be shown to possess some general functional properties that hold approximately. These properties determine and connect the properties of various physical quantities of liquids and gases such as the internal heat of evaporation, intrinsic pressure, Joule Thomson effect, specific heat of liquids, diffusion of gases, viscosity of gases, surface tension, surface energy, coefficients of expansion and compression, heat of formation, the critical quantities, etc. These relations are useful and important, independent of their connexion with the atomic forces. An important property of the force exerted by an atom is that it is measured by the square root of its atomic weight.

The writer has carried out extensive theoretical researches on the subject of molecular forces extending over a number of years, the final outcome of which is this book. An endeavour is made to weld the results obtained into a connected branch of science. It is hoped that it will help to contribute towards placing the subject on a firm basis.

Schenectady, N.Y.,

U S A.

## NOTE.

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The following is a list of the principal symbols used frequently, in a general way, in this book, to which suffixes are attached to indicate any particular meaning :—

## ERRATA.

1. On the right-hand side of equation (77), page 72, *insert* the factor  $(\phi)/m_a^{1/3}$ .
2. On page 113, in the sixth line from the bottom, *read* “ not ” before the word “ to.”
3. In equation (37) on page (51) insert  $m_a$  for  $m$ .
4. *Read*  $\psi_2(T)$  *for*  $\psi(T)$  on page 111, the seventh line.
- 5. In Table XIV., page 68, *read* carbon disulphide *for* fourth substance instead of carbon dioxide.
6. On page 29, Table II., read  $c_a$  for  $A_r$ .
7. On page 122 in the twelfth line *read* U *for* u.

$m_a$	„	absolute molecular weight
N	„	atomic number.
$c_a$	„	atomic attraction constant.
$c_{av}$	„	atomic volume relative to the hydrogen atom.



# **The Atomic and Molecular Forces of Chemical and Physical Interaction in Liquids and Gases, and their Effects.**

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## **CHAPTER I.**

**THE MOLECULAR FORCES IN CONNEXION WITH THE INTERNAL  
HEAT OF EVAPORATION OF LIQUIDS, THE RELATION OF  
CORRESPONDING STATES, THE TEMPERATURE, PRESSURE,  
AND VOLUME OF SUBSTANCES, AND THEIR CRITICAL VALUES.**

1. It was recognized, though perhaps vaguely, by the early scientists and thinkers, that material bodies might possibly exert forces upon one another through the intervening space without the intervention of ponderable matter. The earliest direct experimental evidence of this possibility was probably afforded by the properties of magnetism, long before Isaac Newton's time. It probably helped to lay in Newton's mind the foundation for the idea of explaining the equilibrium of the solar system, and the tendency of matter on the Earth's surface to move towards its centre, by forces of interaction between material bodies acting over a distance. The consequent enunciation of the law of gravitational attraction by Newton in connexion with the motions of the planetary system, which it explained in a striking way, marked an epoch in the subject. The direct measurements of the forces involved carried out later placed the truth of the principle and the law beyond doubt. It was soon recognized, however, that certain properties of matter, which are evidently the outcome of forces acting at a distance, could not be explained by gravitational attraction. These forces give rise to the surface tension of liquids, their internal heat of

evaporation, etc. Since practically gravitational attraction only is in evidence when the attracting bodies are separated by distances greater than a few cms., it follows that the forces giving rise to the foregoing properties of substances must decrease more rapidly with the distance of separation of the attracting bodies, than is the case with gravitational attraction. This attraction, to distinguish it from gravitation attraction, will be called molecular attraction. The law to which it is subject has given rise to a good deal of speculation, mostly in connexion with the equation of state of a substance. It is evident that if the molecular attraction increases more rapidly with decrease of distance between the attracting particles than the gravitational attraction, the former will be large in comparison with the latter for small distances of separation while for large distances of separation the opposite will be the case. Thus under appropriate conditions these attractions may be studied independently of one another.

It can easily be shown that gravitational attraction cannot account for the internal heat of evaporation of a liquid, and the other properties of substances mentioned. Let us calculate, for example, the internal heat of evaporation of a gram of ether at  $0^{\circ}\text{C}$ ., on the supposition that it practically represents the work done against the attraction of the molecules upon one another on separating them an infinite distance, and that gravitational attraction alone is operating. Since the gravitational attraction between two grams of a substance whose centres of mass are separated by unit distance is  $6.658 \times 10^{-8}$  dynes, the attraction between two molecules of ether separated by a distance  $z$  is  $\frac{6.658 \times 10^{-8} (74 \times 1.6 \times 10^{-24})^2}{z^2}$

---

NOTE.—The source of the numerical data used, if not mentioned, is one of the editions of Landolt and Börnstein's Tables.

An account, with references, of the considerations which led to the recognition of other forces of attraction than gravitational, mainly in connection with the equations of state, will be found in Winckelmann's *Handbuch der Physik* under surface tension, continuity of state, and viscosity.



dynes, where  $74 \times 1.6 \times 10^{-24}$  is the mass of an ether molecule. The work done in separating two molecules of ether by an infinite distance when they are initially separated by the distance  $5.44 \times 10^{-8}$  cm., the distance of separation of the molecules of liquid ether at  $0^\circ$  C., is therefore equal to  $3.43 \times 10^{-44}$  erg. If the molecules were initially separated by 100 times this distance the work done would obviously be negligible in comparison with the previous value. Therefore when a molecule is removed from the surface of liquid ether the attraction exerted upon it by the molecules contained in a hemisphere of radius  $100 \times 5.44 \times 10^{-8}$  cm. need only be considered. The energy necessary to remove a molecule is therefore less than  $100^3 \frac{\pi}{2}$  times  $3.43 \times 10^{-44}$  erg, or less than  $10^{-38}$  erg. But according to experiment the energy required is  $4.3 \times 10^{-13}$  erg, which is a much larger value than the foregoing. It follows, therefore, that other forces of attraction besides those of gravitation must exist, which vary much more rapidly with the distance of separation of the attracting bodies than is the case with gravitational attraction.

• It is evident, therefore, that the internal heat of evaporation of a liquid, its surface tension, intrinsic pressure, and its specific heat, must be functions of the law of molecular attraction that exists beside that of gravitation. We must, therefore, look to these quantities to furnish some information about the nature of this law since there are no other quantities which are more directly connected with the molecular forces.

2. The first step necessary in the investigation of the law of molecular attraction is to analyse the energy associated with a molecule in a substance. This energy may be conveniently divided into three parts \*, viz. :—

(1) Potential energy due to the attraction of the molecules upon each other.

\* R. D. Kleeman, *Proc. Camb. Phil. Soc.* xvi. (6) 540 (1912).

(2) Kinetic energy due to the motion of translation of the molecules.

(3) Internal molecular energy, consisting of energy of rotation of the molecule, potential energy due to the attraction of the atoms upon each other, etc.

A change in the internal energy of a mass of matter is thus due to a change in the value of one or more of these quantities, and their joint study is therefore of importance. It will be convenient to consider first the kinetic energy of translation.

It is usually stated as an assumption that the kinetic energy of a molecule in a liquid is the same as that in a gas at the same temperature. The term kinetic energy in this connexion is, however, somewhat ambiguous without any qualifying statements. The subject may be put on a definite basis, from which it will appear that this statement only holds subject to certain restrictions\*.

Suppose that a thermometer is placed in a gas. It will assume the temperature of the gas through being bombarded by the gas molecules. Now, from experience, we know that if a monatomic gas is allowed to expand without doing external work, and its density is so small that the internal work done against the atomic attraction is negligible, the temperature indicated by the thermometer is not altered. This shows that the temperature the thermometer indicates is *independent of the number of molecules impinging per second on each cm.<sup>2</sup> of its surface*. Next let us consider the effect of the material of the bulb on the temperature indicated. A molecule has its velocity increased when it gets into the zone of attraction of the bulb, and each molecule thus impinges on the bulb with a greater velocity than it possesses when not under the influence of an external force. Now suppose the bulb covered with a material which exerts a more powerful attraction on the surrounding gas molecules than the material of the bulb. Each molecule now impinges on the bulb with a much greater

\* R. D. Kleeman, *Phil. Mag.* xxiv. 101 (1912).

velocity than before. But we know from experience that the temperature indicated by a thermometer is independent of its material. It appears, therefore, that the temperature indicated by a thermometer placed in a gas is regulated by *the velocity the molecules have when not under the influence of an external force.*

Suppose next that the thermometer is placed in a liquid. Now a large number of points exist in a liquid (which like the molecules are in motion) at which the forces of the surrounding molecules neutralize each other. It follows then from the foregoing considerations that the thermometer indicates a temperature corresponding to the velocity of a molecule when passing through one of these points. This velocity is equal to that which it has in the gaseous state at the same temperature.

The velocity at other points in the liquid is greater than this velocity. For the effect of molecular attraction is to make the molecules in a mass of matter approach one another on collision with a greater velocity than they would have if they did not possess any attraction upon one another. It follows, therefore, that the *average minimum velocity* of a molecule corresponds to its velocity in the gaseous state at the same temperature, while the *total average velocity* is larger and, as we will see later, much larger than this velocity\*.

The average minimum velocity, or the average kinetic energy velocity  $V$ , is given by the expression  $\left(\frac{3RT}{m}\right)^{1/2}$ , where  $T$  denotes the absolute temperature,  $m$  the mass of a molecule relative to that of a hydrogen atom, and  $R$  the gas constant whose value is  $8.315 \times 10^7$  †.

3. Let us next consider the potential energy of attraction of a substance. Suppose that the molecules of a mass of

\* See also *A Kinetic Theory of Gases and Liquids*, by R. D. Kleeman, (New York: John Wiley & Sons).

† This need hold only up to small but *finite* molecular concentrations, as far as the purpose of this book is concerned. See *Z. f. anorg. u. allgem. Chemie*, clxvi. 284 (1931).

matter are separated by an infinite distance from one another, keeping the temperature constant, by supplying an amount of heat, or heat and mechanical work. A certain amount of the energy supplied is expended in overcoming the attraction of the molecules upon each other. Therefore with every gram of the substance is associated before the process of separation a quantity of potential energy of molecular attraction which will be denoted by  $P$ , and after the process a limiting quantity of potential energy which will be denoted by  $P'$ . The difference  $P' - P$ , which will be denoted by  $U_c$ , is the amount of energy expended in overcoming the molecular attraction during the process.

In order to obtain  $U_c$  from the law of molecular attraction it is necessary to investigate, first, whether its value is influenced by the motion of translation of the molecules, and what must be the mean distribution of the molecules for purposes of calculation. Consider the energy expended on a molecule in overcoming the molecular attraction in moving it instantaneously to an infinite distance from the substance. It is obvious that the work done depends on the position of the molecule relatively to the other molecules at the instant before its removal. But the mean value of the energies expended in removing it at successive intervals of time  $\partial t$  during a large value of  $t$  (after each removal the molecule is supposed to be returned instantaneously to its previous position), is a constant which is the same for each molecule. As far as the potential energy of molecular attraction of a substance is concerned, we may therefore replace the substance by one in which the molecules are fixed in space in such a way that the change in potential energy for each molecule on being removed is equal to the above mean value. This distribution in space is obtained when it satisfies the following conditions:—

(1) The resultant force exerted on a molecule by the surrounding molecules is zero—which corresponds to each

molecule in a pure substance being similarly situated with respect to the surrounding molecules.

(2) The potential energy of a mass of matter at constant density and subject to condition (1), due to molecular attraction, is a minimum.

(3) A mixture of different substances is symmetrically divided into cells of the same kind and magnitude in each of which the molecules are relatively distributed in the same way. The nature of the distribution of the molecules in a cell may vary, however, from one part of the cell to another.

Condition (1) expresses the fact that the molecules in a substance are in equilibrium, which would be the case if each molecule in its mean position is not under the action of any force. Condition (2) expresses the mechanical principle that the equilibrium of a rational mechanical system is stable when the potential energy, or force function, is a minimum. Condition (3) expresses that the molecules in a homogeneous mixture will be as evenly as possible distributed. This distribution cannot in general be such that it is of a symmetrical character for each of the constituents considered separately. The most even distribution that can be obtained, it will be evident upon reflection, is that which satisfies this condition.

The geometrical distribution of the molecules in a pure substance satisfying the foregoing conditions is a simple one. On reflection it will be found that the molecules are situated at the points of intersections of three systems of parallel equidistant planes which are at right angles to one another.

Since a molecule in its mean position is not under the action of a force tending to displace it, its velocity (in this position) is the same as that which it has in the gaseous state at the same temperature (Art. 2). Therefore on removing the molecule at *constant temperature* from the substance energy is expended only in overcoming the molecular attraction, and changing the internal molecular energy.

This will perhaps appear clearer if we suppose that the

substance is expanded till its volume is infinite, and then compared with its initial state, supposing the molecules occupy their mean positions in both states. The velocity of each molecule corresponding to its mean position remains unchanged. No work was therefore done during the expansion which changed the kinetic energy of the molecules.

Thus a part of the energy associated with the molecules in a substance consists of kinetic energy of translation, which depends only on the temperature of the substance. Another part consists of potential energy of molecular attraction and repulsion, whose change between given limits, one of which is the perfectly gaseous state, is denoted by  $U_a$ . The third part consists of internal molecular energy whose nature will now be considered more closely.

4. The internal energy of the molecules of a gram of a substance will be denoted by  $u$ . Let us first consider the nature of this quantity when the substance is in the state of a perfect gas, in which case it will be denoted by  $u_a$ . Obviously it must then consist of kinetic energy of rotation, vibration, etc., of the atoms of each molecule, and of potential energy of attraction due to the attraction of the atoms in each molecule upon each other, and of the parts of an atom upon each other, which energies exist apart from the kinetic energy of translation of each molecule as a whole, and the potential energy due to the attraction of the molecules upon each other. This quantity can immediately be connected with  $c_v$ , the specific heat per gram at constant volume when the substance is in the state of a perfect gas. Thus we have directly that

$$c_v = \left( \frac{\partial u_a}{\partial T} \right)_v + \frac{3R}{2m}, \quad . . . . . (1)$$

where  $\frac{3R}{2m}$  denotes the change in kinetic energy of the molecules of a gram of substance of relative molecular weight  $m$  when its temperature is raised one degree (Art. 3) and  $\left( \frac{\partial u_a}{\partial T} \right)_v$  the corresponding change in internal molecular energy.

The measurements of the quantity  $c_v$  that have been carried out indicate that  $\left(\frac{\partial u_a}{\partial T}\right)_v$  is independent of the volume  $v$  of the gas if it obeys Boyle's Law \*. It follows, therefore, that

$$\left(\frac{\partial u_a}{\partial v}\right)_T = 0$$

holds also under these conditions. The average internal energy of a molecule in the perfectly gaseous state is therefore independent of the number of collisions it undergoes per second with other molecules. The sign of  $\left(\frac{\partial u_a}{\partial T}\right)_v$  is usually positive. That it is not zero shows that the internal energy of a molecule is, however, influenced by the violence of its collision with other molecules.

If the internal energy of a molecule consists partly of potential energy of attraction of the atoms upon one another, we should expect that it would depend on the complexity and chemical constitution of the molecule. Information on this point can be obtained, as is known, from the ratio of the specific heat at constant pressure to that of constant volume of gases. The specific heat at constant volume of a gas whose molecules do not possess molecular internal energy which depends on the temperature, is equal to the kinetic energy of translation of a gram of molecules, which we have seen is equal to  $\frac{3R}{2m}$ . The specific heat at constant pressure is accordingly

$$p\left(\frac{\partial r}{\partial T}\right)_p + \frac{3R}{2m} \text{ or } \frac{5R}{2m}, \text{ since } pv = \frac{RT}{m}.$$

The ratio of the two specific heats thus is  $5/3$  or  $1.666$ . Therefore, if the molecules of a gas possess molecular internal energy which depends on the temperature, the ratio would be smaller than  $1.666$ . Table I. gives this ratio for a few gases of different complexities. It will be seen that it decreases with

\* This probably holds only approximately even under ideal conditions (*loc. cit.*).

the complexity of the gas, as we might expect. For a non-atomic gas it is equal to 1.6666, showing that an isolated atom contains little or no atomic internal energy which depends on the temperature.

TABLE I.

Name of gas.	Chemical formula.	Ratio of the specific heats.
Mercury .....	Hg	1.666
Argon .....	Ar	1.63
Carbon monoxide .....	CO	1.403
Hydrochloric acid .....	HCl	1.398
Oxygen .....	O <sub>2</sub>	1.41
Hydrogen .....	H <sub>2</sub>	1.41
Nitrogen .....	N <sub>2</sub>	1.41
Chlorine .....	Cl <sub>2</sub>	1.336
Carbon dioxide .....	CO <sub>2</sub>	1.311
Water .....	H <sub>2</sub> O	1.33
Chloroform .....	CHCl <sub>3</sub>	1.11
Alcohol .....	C <sub>2</sub> H <sub>6</sub> O	1.13
Ether .....	C <sub>4</sub> H <sub>10</sub> O	1.03

It can be shown that it is highly probable that the atomic configuration of a molecule in a substance depends on its density, and that therefore the internal molecular energy would be similarly affected. Thus we have seen in the previous article that in calculating the amount of energy expended in overcoming molecular attraction in separating the molecules of a mass of substance by an infinite distance from one another, we may suppose the molecules devoid of motion and distributed in space in positions which may be called their mean positions. One of the conditions determining this distribution is that the force on each molecule by the surrounding molecules should be zero. It follows, therefore, that if the molecules consist of points they would be, whatever the density of the substance, in the same condition at their mean positions as in the gaseous state, as far as the dissociating action of the surrounding molecules is concerned. They would therefore possess the same internal energy as in the gaseous state. But since it is fairly certain that the atoms of a molecule are not concentrated at a point, the internal energy must be influenced



by the surrounding molecules. Thus when a molecule is in its mean position the effect of the surrounding molecules would be to produce a radial force acting outwards from some point in the molecule, which partly neutralizes the attraction between the atoms. This would change the configuration of the molecule and consequently its internal energy from that which it would possess in the perfectly gaseous state. Further, the internal energy of a molecule is likely to be affected by the nature of its collisions with other molecules, and it might thus retain, after taking up its mean position, a part of the change in internal energy caused by collisions undergone previously. The nature of the collision of a molecule in a liquid obviously differs from that in a gas. The effect of molecular collision on the internal energy of a molecule is therefore likely to depend on the density of the substance.

It becomes of importance therefore to obtain the precise meaning of the quantity  $u$  of a substance at a density such that the molecules are under the influence of each other's attraction. Suppose that (by means of some external agent) the *configuration* of each molecule in the substance is changed at constant volume and temperature of the substance to that which it would have in the perfectly gaseous state. Let  $\partial u$  denote the resultant change in *internal molecular energy* per gram of substance. This may be divided into two parts,  $\partial u_s$  and  $\partial u_i$ , where  $\partial u_s$  denotes the change in energy that would occur if the molecules were shielded from each other's attraction, and  $\partial u_i$  the *additional* change due to the molecules being under each other's influence.  $\partial u_s$  evidently represents the change in potential energy of the molecule due to the attraction and repulsion of the different parts of a molecule upon each other, and  $\partial u_i$  the change in potential energy due to the forces the external molecules exert on these parts. Now it can be shown that  $\partial u_i$  is equal to the change that takes place in  $U_e$  on changing the configuration of the molecules as described, where  $U_e$ , as usual, denotes the energy expended against molecular attraction in separating the molecules an infinite distance from one another.

Thus suppose that the molecules are passed through the following cycle:—

Let the configuration of the molecules of the substance be changed in the same way as before, giving rise to a change in internal energy equal to  $\partial u_s + \partial u_i$ . Now let the substance be expanded at constant temperature till it is in the perfectly gaseous state, keeping the molecular configuration constant during the process. Let  $U_1$  denote the energy absorbed, which consists only of work done against molecular attraction. Now change the configuration of the molecule back to what it was before the beginning of the cycle. The energy absorbed is equal to  $-\partial u_a$  according to the definition of  $u_a$ . Now compress the substance at constant temperature till it has regained its original volume, keeping the molecular configuration constant during the process, and let  $-U_2$  denote the energy absorbed. The substance has been passed through a complete cycle, and the change in internal energy is therefore equal to zero, that is

$$\partial u_s + \partial u_i + U_1 - \partial u_a - U_2 = 0,$$

or

$$\partial u_i = U_2 - U_1 = \partial U_c, \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where  $\partial u_s = \partial u_a$  since  $\partial u_s$  and  $\partial u_a$  correspond to the same change in molecular configuration and represent the changes in the internal energy of the molecules when not influencing each other—in the gaseous state on account of the magnitude of their distance of separation, and in the condensed state on being shielded from each other's influence.

The preceding equation states that if the configuration of the molecules of a substance is changed on change of volume, the part of the change in internal molecular energy *due to the presence of the forces of attraction and repulsion of the surrounding molecules* appears as a change in the potential energy of molecular attraction and repulsion. *Therefore the quantity  $u - u_a$ , or the change in internal molecular energy of a gram of molecules on separating them an infinite distance from one another, is equal to the change in energy at constant*

*volume of the substance which the molecules would undergo if they were shielded from the forces they exert upon one another, and their configuration be changed to that which they have in the perfectly gaseous state.*

If  $Q_1$  denotes the total change in internal energy, or the heat absorbed minus the external work done, on expanding a substance at constant temperature till its volume is infinitely great, we have

$$Q_1 = U_\infty - (u - u_\infty) \dots \dots \dots (2)$$

according to the results of this and the previous Articles. For a small change in volume of the substance we would accordingly have

$$\partial Q_1 = \partial U_\infty - \partial u \dots \dots \dots (3)$$

Of these quantities  $Q_1$  only can be measured directly. Therefore the relative values of  $U_\infty$  and  $u - u_\infty$  of a substance cannot be determined directly in practice. We would expect, however, from general considerations that  $u - u_\infty$  should in all cases be small in comparison with  $U_\infty$ . Some evidence that this is so will be pointed out, though it is not very strong\*.

Suppose that a homogeneous substance in a cylinder provided with a piston is suddenly expanded, and that two phases of the substance are formed. If the temperature of the substance is raised before each expansion a point is ultimately reached when the substance remains homogeneous on expansion, which corresponds to the critical point. It is evident from a consideration of this operation that at this point the kinetic energy (Art. 2) is equal to  $U_\infty$ , or

$$\frac{1}{2} m V^2 = \frac{3RT}{2m} = U_\infty \dots \dots \dots (4)$$

The internal heat of evaporation  $L$  of a liquid, which is related to  $U_\infty$ , according to Clapeyron's equation is given by

$$L = \left( T \frac{dp}{dT} - p \right) \left( \frac{1}{\rho_2} - \frac{1}{\rho_1} \right), \dots \dots \dots (5)$$

where  $\rho_1$  and  $\rho_2$  denote the densities of the liquid and vapour

\* R. D. Kleeman, *Proc. Camb. Phil. Soc.* xvii. (5), 402 (1914).

respectively at the temperature  $T$  and pressure  $p$ . At low temperatures when  $\rho_2$  is small the equation may be written

$$L_c = \left( T \frac{dp}{dT} - p \right) \frac{1}{\rho_2}, \quad . . . . . (6)$$

where  $L_c$  now corresponds to the change in internal energy on separating the molecules an infinite distance from each other, whence

$$L_c = U_c - (u - u_a). \quad . . . . . (7)$$

If equation (6) also gives the change in internal energy corresponding to infinite molecular separation at the critical point, which is highly likely, we obtain

$$U_c - (u - u_a) = \frac{1}{\rho_c} \left( T \frac{dp}{dT} - p \right)_{p=p_c}, \quad . . . . . (8)$$

where  $\rho_c$  denotes the critical density and  $p_c$  the critical pressure. From this equation, making use of the equation

$$\left( \frac{dp}{dT} \right)_{p=p_c} = 7.5 \frac{p_c}{T_c}, \quad . . . . . (9)$$

which has been shown to hold by Dieterici \*, and the equation  $p_c = \frac{\rho_c RT_c}{3.7m}$ , which has been shown to hold at the critical point, we obtain

$$U_c - (u - u_a) = 1.76 \frac{RT_c}{m}. \quad . . . . . (10)$$

From equations (10) and (4) applied to the critical point we deduce

$$u - u_a = -.26 \frac{RT_c}{m},$$

and hence

$$u - u_a = -.17 U_c, \quad . . . . . (11)$$

or  $u - u_a$  is small in comparison with  $U_c$ . In what follows  $u - u_a$  will therefore be neglected in comparison with  $U_c$ .

5. Given the law of attraction between the molecules of a substance, the work done in overcoming the molecular

\* *Ann. d. Phys.* xii. 144 (1903).

attraction when the volume of the substance is changed, can evidently be calculated; conversely, if the law be not known, some information about its nature may be obtained from an investigation of thermal and other data involving molecular attraction. The writer has obtained the law of attraction in a fundamental form by means of an investigation of this nature\*. It may be stated in its general form as follows:—The attraction between two molecules of the same kind in a substance at the absolute temperature  $T$  and separated by the distance  $z$  is given by

$$\phi\left(\frac{T}{T_c}, \frac{z}{x_c}\right) \cdot \frac{(\Sigma c_a)^2}{z^5}, \quad . . . . . (a)$$

where  $x_c$  denotes the minimum distance of separation of two molecules in the liquid state at the critical temperature  $T_c$ .  $\Sigma c_a$  denotes the sum of a number of constants each of which refers to one of the atoms in a molecule, and  $\phi\left(\frac{T}{T_c}, \frac{z}{x_c}\right)$  is a function of the ratios  $\frac{T}{T_c}$  and  $\frac{z}{x_c}$ . For the present we are not concerned with the exact nature of this function. It will for shortness be denoted by  $(\phi)$ . The quantity  $\Sigma c_a$  will be called the molecular attraction constant, and  $c_a$  the attraction constant of an atom†. It will be noticed that if  $(\phi)$  were a constant, or a quantity independent of  $T_c$  and  $x_c$ , the attraction

\* *Phil. Mag.* p. 491, Oct. 1909; p. 901, Dec. 1909; p. 783, May 1910.

† Einstein has previously used (*Annal. der Physik*, iv. p. 513, 1901) the theorem that the attraction between two molecules is proportional to the product of two constants, each of which depends on the nature of one of the molecules, and that each constant consists of the sum of a number of constants referring to the atoms of the corresponding molecule. He obtained negative values for some of the atomic constants, through not taking into account the property of corresponding states of substances. This result is not likely to hold, since it indicates that an atom with a negative constant repels an atom with a positive constant. If the property of corresponding states is taken into account, however, as the writer has done, the atomic constants assume positive values which are connected, we shall see, in a definite way with the atomic weights.

between two atoms or molecules separated by a given distance would be proportional to the product of their attraction constants.

The foregoing law of attraction is supposed to apply to a pair of molecules which form part of a homogeneous mass of liquid or gaseous matter. The two molecules are in that case constantly under the influence of the other molecules which might conceivably affect their attraction upon each other. Moreover, on account of the rotations round their centres of gravity which these two molecules undergo, they would be attracting each other under continually changing aspects. The law of attraction obtained under these conditions is therefore, in a sense, a mean law, since the forces of attraction and repulsion of a molecule are probably not distributed symmetrically around it. This law is probably very different from the one that would be obtained if two molecules could be isolated and kept facing each other in the same way. The former law is of greater importance than the latter, since we are always in practice dealing with a homogeneous group of molecules.

The points in space which indicate the distribution of the molecules in a liquid in connexion with considerations of potential energy of attraction (Art. 2) are evidently the centres of attraction of the molecules, or the points at which the forces of attraction of the molecules appear to be located. The quantity  $z$  in the above law of molecular attraction is therefore the distance between these centres of two molecules.

If the attraction of one molecule on another may be screened to a certain extent by the presence of one or more molecules, this would be taken into account in the foregoing law.

6. The law stated in the previous Article will now be used to obtain a formula\* for the value of  $U_c$  (Art. 2) for a gram of substance of given density. Its value is obviously not

\* R. D. Kleeman, *Proc. Camb. Phil. Soc.* xvi. (7) 583 (1912).

affected by the mass of matter under consideration unless it be of microscopical magnitude.

We must suppose for mathematical reasons, however, in obtaining the correct mathematical expression for  $U_0$ , that we are dealing with an infinitely large mass of substance. Let us suppose that it is in the form of a cube, and that the systems of parallel planes by means of which the distribution of the molecules is defined in Art. 3 are taken parallel to the sides of the cube. Suppose that a layer of molecules is moved to infinity, and the molecules of the layer then separated by an infinite distance from one another by removing the molecules of each row consecutively, beginning at one edge of the layer. Let the process be repeated till nothing of the cube is left. The average work done per gram of substance is the value of  $U_0$ . It is the same as if the cube were expanded till its volume is increased an infinite number of times.

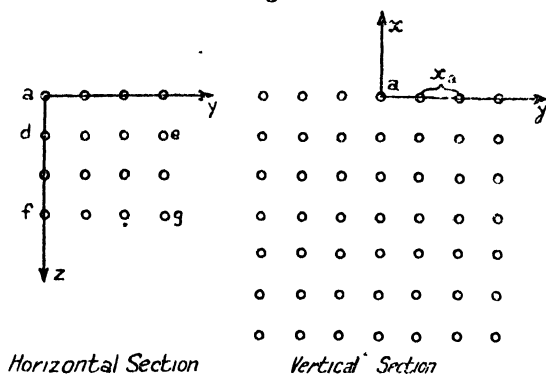
Instead of removing successively the layers of molecules we may suppose them to remain in their position and the molecules of each layer separated in the same way as before. It will be evident, on consideration of the foregoing process, that the *average* work done in removing a molecule of the cube to infinity is equal to that done in removing the centre molecule of one of the surface layers of the cube, supposing that half of the row of molecules in which this molecule lies and all the molecules of the layer on one side of this row, to be absent.

Let this molecule be denoted by  $\alpha$  in fig. 1, which gives in part a horizontal and a vertical section of the cube. Let the position of the molecule be taken as origin of coordinates, and the axes taken parallel to the edges of the cube, the notation of the axes being shown in the figure. Let the distance between two consecutive molecules parallel to one of the edges of the cube be denoted by  $x_a$ .

Consider the molecule  $\alpha$  placed on the axis of  $x$  at a distance  $nx_a$  from the origin. Its coordinates are now  $(nx_a, 0, 0)$ . Let the coordinates of a molecule in the cube be  $(wx_a, ux_a, vx_a)$ ,

where  $w$ ,  $u$ , and  $v$ , it will be noticed, can only assume zero and integral values \*. The component of attraction of this molecule

Fig. 1.



on the molecule  $a$  along the axis of  $x$  is therefore according to the law of attraction given in Art. 5 equal to

$$\phi\left(\frac{T}{T_c}, \frac{z}{x_c}\right) \cdot \left(\frac{nx_a + wx_a}{z}\right) \frac{(\sum c_a)^2}{z^5},$$

where  $z$  is the distance of separation of the two molecules and  $\frac{nx_a + wx_a}{z}$  the cosine of the angle between the axis  $x$  and the line joining the two molecules. The value of  $z$  from geometrical considerations is given by the equation

$$z = \sqrt{\{(nx_a + wx_a)^2 + u^2 x_a^2 + v^2 x_a^2\}} = x_a \sqrt{\{(n+w)^2 + u^2 + v^2\}},$$

which for shortness we will write  $z = x_a k_c$ .

The work done in moving the molecule  $a$  against the attraction of the remaining molecules of the cube along the axis of  $x$  to infinity may be divided into three parts. One of them is the work done against the attraction of the row of molecules  $c_1 c_2$  (consisting of half a row of molecules minus the molecule  $a$ ), and which is equal to

$$\sum_{v=1}^{\infty} \int_0^{\infty} (\phi) \cdot (\sum c_a)^2 \frac{nx_a}{z^6} \cdot d(nx_a) = \sum_{v=1}^{\infty} \int_0^{\infty} (\phi) \frac{(\sum c_a)^2}{x_a^4} \frac{n}{(n^2 + v^2)^3} dn.$$

\* For convenience a distance measured along the  $x$  axis will always be taken positive.



Another part is the work done against the attraction of the layer of molecules  $d, e, f, g$  (which is half the surface layer of the cube minus one row), and which is equal to

$$\sum_{v=-\infty}^{v=\infty} \sum_{u=1}^{u=\infty} \int_0^{\infty} (\phi)(\Sigma c_a)^2 \frac{(n x_a)}{z^6} \cdot d(n x_a) \\ = \sum_{v=-\infty}^{v=\infty} \sum_{u=1}^{u=\infty} \int_0^{\infty} (\phi) \frac{(\Sigma c_a)^2}{x_a^4} \frac{n}{(n^2 + u^2 + v^2)^3} \cdot dn.$$

The remaining part is the work done against the attraction of the molecules of the cube minus the surface layer, which is equal to

$$\sum_{v=-\infty}^{v=\infty} \sum_{u=-\infty}^{u=\infty} \sum_{w=1}^{w=\infty} \int_0^{\infty} (\phi) \frac{(\Sigma c_a)^2}{x_a^4} \frac{n+w}{\{(n+w)^2 + u^2 + v^2\}^3} \cdot dn.$$

Each of the foregoing expressions is of the form

$$\psi\left(\frac{T}{T_c}, \frac{x_a}{x_c}\right) \frac{(\Sigma c_a)^2}{x_a^4},$$

since

$$(\phi) = \phi\left(\frac{T}{T_c}, \frac{z}{x_c}\right) \quad \text{and} \quad z = x_a k_c.$$

The sum of the above three expressions may therefore be written

$$\phi_1\left(\frac{T}{T_c}, \frac{x_a}{x_c}\right) \frac{(\Sigma c_a)^2}{x_a^4},$$

where  $\phi_1\left(\frac{T}{T_c}, \frac{x_a}{x_c}\right)$  is a function of the ratios  $\frac{T}{T_c}$  and  $\frac{x_a}{x_c}$ . If  $\rho$  denotes the density of the substance,  $\rho_c$  the critical density, and  $m_a$  the absolute molecular weight of a molecule,

$$x_a = \left(\frac{m_a}{\rho}\right)^{1/3} \quad \text{and} \quad x_c = \left(\frac{m_a}{\rho_c}\right)^{1/3}.$$

Therefore, since there are  $1/m_a$  molecules in a gram of substance, we may write

$$U_c = \phi_2\left(\frac{T}{T_c}, \frac{\rho}{\rho_c}\right) \frac{\rho^{1/3}}{m_a^{1/3}} (\Sigma c_a)^2. \quad \dots \quad (12)$$

The internal heat of evaporation  $L$  of a substance is given by

$$L = U_{c1} - U_{c2} - (u_1 - u_2). \quad \dots \quad (13)$$

where the suffixes 1 and 2 refer to the liquid and vapourous states respectively in contact with one another.

From Art. 3 it follows that  $(u_1 - u_2)$  is small in comparison with  $(U_1 - U_2)$  and therefore we have very approximately

$$L = U_{o1} - U_{o2} \quad . \quad . \quad . \quad . \quad . \quad . \quad (14)$$

or, finally,

$$L = \left\{ \phi_2 \left( \frac{T}{T_o}, \frac{\rho_1}{\rho_o} \right) \cdot \rho_1^{4/3} - \phi_2 \left( \frac{T}{T_o}, \frac{\rho_2}{\rho_o} \right) \cdot \rho_2^{4/3} \right\} \frac{(\Sigma c_a)^2}{m_a^{7/3}} \quad . \quad . \quad (15)$$

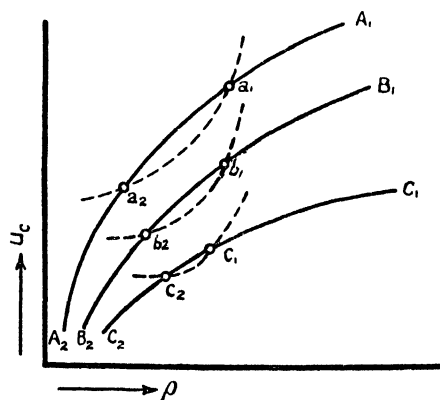
by means of equation (12), which gives an expression for  $U_o$ .

7. It can be shown that  $U_o$  must be considered a function of the two independent variables, temperature and density, if there exists no proof to the contrary, and no assumptions are introduced in our reasoning. Thus consider a mass of matter of density  $\rho$  at the temperature  $t_1^\circ$ , and let the energy necessary to separate the molecules an infinite distance from one another be denoted by  $U_o'$ . Now let the temperature of the matter be raised to  $t_2^\circ$ , keeping the volume of density of the matter constant, and let  $U_o''$  denote the corresponding value of  $U_o$ . Now the value of  $U_o''$  is not necessarily equal to  $U_o'$ , for the attraction of the molecules upon one another *may* depend on the temperature. We must take this possibility into account unless there exists definite evidence to the contrary, or that  $U_o$  may change independently of  $\rho$ . Now  $U_o$  is obviously a function of  $\rho$  when the temperature is kept constant, and thus  $U_o$  must be considered a function of the two independent variables  $\rho$  and  $T$ , if, as stated before, we cannot prove the contrary, and no assumptions are introduced. That  $U_o$  may change with the temperature when the volume of the matter is kept constant is highly probable. Such a change could be brought about by a change in the configuration of the atoms of each molecule with rise of temperature. A change in atomic configuration very likely occurs under these circumstances, since the specific heat of a molecule in the gaseous state and its change with change of temperature depends on the mole-

cular complexity, as is shown by Table I. in Art. 4. Evidence of a more direct nature that the molecular attraction is a function of the temperature will be found in Chapter VI.

Since  $U_c$  must be considered a function of two independent variables, it can be shown that it is mathematically impossible to discover its exact form from data of internal evaporation of liquids \*. Thus let the curve  $A_1 A_2$  in fig. 2 denote the graph connecting  $U_c$  and  $\rho$  of a substance corresponding to a constant temperature  $T_1$ , these quantities being connected by an equation of the form  $U_c = \psi(\rho, T)$  as we have seen. Let the curve  $B_1 B_2$  be the graph corresponding to a constant temperature  $T_2$ , etc., the quantities  $T_1, T_2, T_3, \dots$ , being in ascending order of

Fig. 2.



magnitude. Let the abscissæ of the points  $a_1, b_1, c_1, \dots$  correspond to the densities of the substances in the liquid state in contact with its saturated vapour at the temperatures  $T_1, T_2, T_3, \dots$ , and the abscissæ of the points  $a_2, b_2, c_2, \dots$  correspond to the densities of the saturated vapour. The heat of evaporation of the liquid at the temperature  $T_1$  is then given by the difference between the ordinates of the points  $a_1$  and  $a_2$ , and the heat of evaporation at the temperature  $T_2$  by the difference between the ordinates of the points  $b_1$  and  $b_2$ , and so on. It will now be evident that the equation giving the

\* R. D. Kleeman, *Phil. Mag.* xxi. 83 (1911).

internal heat of evaporation in terms of  $\rho$  and  $T$  represents a series of curves of which  $T$  is the parameter, passing through the points  $a_1, a_2, b_1, b_2, \dots$ , as shown in the figure by a number of dotted curves, but which need not necessarily coincide with any other points or parts of the curves  $A_1A_2, B_1B_2, \dots$ . It is obvious, then, that an infinite number of sets of such curves can be found, each of which corresponds to a different formula for the heat of evaporation. Therefore the form of the function  $U_e$ , and consequently that of the law of molecular attraction, cannot be determined from an equation expressing the internal heat of evaporation in terms of  $\rho$  and  $T$ . Each of the various latent heat equations corresponds to a different form of  $U_e$ , and therefore to a different form for the law of molecular attraction. This result may also be expressed by saying that each of the mathematically correct expressions for  $U_e$ , and the law of molecular attraction, determined from an equation giving the heat of evaporation in terms of  $\rho$  and  $T$ , must contain an arbitrary function.

The investigation in this Article shows that it is mathematically impossible to obtain the correct expression for  $U_e$  of a substance at a given density and temperature from data of the internal heat of evaporation. Therefore if these data are taken into account it must be done in such a way that, as far as these data are concerned, the expression for  $U_e$  (and consequently the law of molecular attraction) is left arbitrary, or  $\rho$  contains an arbitrary function. In that case only can we be sure that the deductions made are mathematically sound.

It follows, therefore, that if the law of molecular attraction suggested in Art. 5 be true, and the latent heat equation (15) derived from it be applied to the facts, the form of the function ( $\phi$ ) would be left arbitrary. But it is evident that the nature of the constants  $c_a$  would be determined if the data are sufficiently extensive. Before carrying out this determination it will be of advantage to deduce some further relations that follow from the proposed form of the law of molecular attraction.

8. If the various expressions for the internal heat of evaporation that can be found according to the previous Article are equated with one another, an infinite number of equations are obtained connecting the temperature  $T$  with the densities  $\rho_1$  and  $\rho_2$  of the liquid and the saturated vapour. But two only are independent. We know from the facts that if one of the foregoing three quantities is given, the corresponding values of the two other quantities become determinate, or each of these quantities may be expressed in terms of one of them. *Therefore any two of the foregoing equations give the relations between the quantities  $\rho_1$ ,  $\rho_2$ , and  $T$ .*

If the variables in the other equations be expressed in terms of one of them from these two equations, some of the equations may become identities, while those that do not must each have an infinite number of roots giving an infinite number (though not necessarily the whole number) of the physically possible values of the variable.

If the law of molecular attraction has the form given in Art. 5, we have seen in the previous Article that the form of the function  $(\phi)$  in the law is left arbitrary by a consideration of the data of heat of evaporation. The various latent-heat equations satisfying the facts therefore correspond to different forms of  $(\phi)$ . It follows, therefore, from equation (15) that the equations obtained on equating the various latent-heat equations (which correspond to various forms of  $(\phi)$ ) are of the type

$$\begin{aligned} \phi_2' \left( \frac{T}{T_c}, \frac{\rho_1}{\rho_c} \right) \cdot \left( \frac{\rho_1}{\rho_2} \right)^{4/3} - \phi_2' \left( \frac{T}{T_c}, \frac{\rho_2}{\rho_c} \right) &= \phi_2'' \left( \frac{T}{T_c}, \frac{\rho_1}{\rho_c} \right) \cdot \left( \frac{\rho_1}{\rho_2} \right)^{4/3} \\ - \phi_2'' \left( \frac{T}{T_c}, \frac{\rho_2}{\rho_c} \right) &= \phi_2''' \left( \frac{T}{T_c}, \frac{\rho_1}{\rho_c} \right) \cdot \left( \frac{\rho_1}{\rho_2} \right)^{4/3} - \phi_2''' \left( \frac{T}{T_c}, \frac{\rho_2}{\rho_c} \right) \quad \dots \quad (16) \end{aligned}$$

The form of these equations is the result of the form of the function  $(\phi)$  in the law of molecular attraction, which is a function of the ratios  $\frac{T}{T_c}$ ,  $\frac{z}{z_c}$ . Any two of these equations therefore express \* the general nature of the relations between

\* R. D. Kleeman, *Phil. Mag.* xxi, 325 (1911).

the quantities  $\rho_1$ ,  $\rho_2$ , and  $T$  in conformity with the law of molecular attraction.

9. On eliminating  $T_c$ , the critical temperature, from any two of the foregoing equations, we obtain an equation from which  $\rho_c$ , the critical density, can be calculated from any convenient density and temperature data. Similarly, an equation can be obtained from which  $T_c$  can be calculated. These equations are the fundamental equations for determining  $T_c$  and  $\rho_c$  of a liquid from its properties at any given temperature.

10. If we express the temperature and density of a liquid and of its saturated vapour in terms of their critical values, that is, write

$$\rho_1 = e_1 \rho_c, \quad \rho_2 = e_2 \rho_c, \quad \text{and} \quad T = e_3 T_c$$

and substitute in equations (16), they become

$$\begin{aligned} \phi_2'(e_3, e_1) \cdot \left(\frac{e_1}{e_2}\right)^{4/3} - \phi_2'(e_3, e_2) &= \phi_2''(e_3, e_1) \cdot \left(\frac{e_1}{e_2}\right)^{4/3} - \phi_2''(e_3, e_2) \\ &= \phi_2'''(e_3, e_1) \cdot \left(\frac{e_1}{e_2}\right)^{4/3} - \phi_2'''(e_3, e_2). \quad \dots \quad (17) \end{aligned}$$

These equations do not contain any quantity depending on the nature of the liquid. Each of the quantities  $e_1$ ,  $e_2$ , and  $e_3$  can thus be expressed in terms of one of the remaining two, since two of the equations are independent according to Art. 8. It follows, therefore, that if the value of one of these quantities is taken the same for each of a number of liquids in contact with their saturated vapours, the values of the remaining quantities will be the same for each substance—in other words, if the values of  $\rho_1/\rho_c$  or  $\rho_2/\rho_c$  be plotted against the values of  $T/T_c$  the same curve would be obtained for each substance. This relation is a particular case (referring to liquids in contact with their saturated vapour) of what is known as the property of corresponding states.

A similar relation can be deduced applying to matter in any state which, in general, is then completely defined by a knowledge of two of the variables, temperature, pressure, and

density, instead of by one as in the case of a liquid in contact with its saturated vapour. Thus from thermodynamics we have

$$\left(\frac{\partial Q}{\partial p}\right)_T = -T \left(\frac{\partial v}{\partial T}\right)_p, \quad . . . . . (18)$$

where  $\partial Q$  is the amount of heat absorbed by a mass of matter of volume  $v$  at a constant temperature 'T' when the external pressure is increased by  $\partial p$ . Now

$$\partial Q = -\partial U_c + \partial u + p \cdot \partial v,$$

where  $p \cdot \partial v$  denotes the external work done when the volume of the substance is increased by  $\partial v$ . According to Art. 3, the quantity  $\partial u$  may be neglected in comparison with  $\partial U_c$ . The expression for  $U_c$  given by equation (12) in Art. 6 may be written  $U_c = HC/v^{4/3}$ , where

$$\rho = 1/v, \quad C = \frac{(\sum c_a)^2}{m_a^{7/3}},$$

and  $H$  is a quantity obeying the relation of corresponding states. The foregoing thermodynamical equation may now be written

$$\left\{ C \left[ \left(\frac{\partial H}{\partial v}\right)_T \frac{1}{v^{4/3}} - \frac{4}{3} \frac{H}{v^{7/3}} \right] + p \right\} \left(\frac{\partial v}{\partial p}\right)_T = -T \left(\frac{\partial v}{\partial T}\right)_p.$$

Let us now express the quantities  $p$ ,  $v$ , and  $T$  (which now refer to all possible states of matter) in terms of their critical values thus :

$$p = r_1 p_c, \quad v = r_2 v_c, \quad \text{and} \quad T = r_3 T_c.$$

The equation then becomes

$$\frac{C}{v_c^{7/3} p_c} \left\{ \left[ \left(\frac{\partial H}{\partial v}\right)_{r_3} r_2 - \frac{4}{3} H \right] \frac{1}{r_2^{7/3}} + r_1 \right\} \left(\frac{\partial r_2}{\partial r_1}\right)_{r_3} = -r_3 \left(\frac{\partial r_2}{\partial r_3}\right)_{r_1},$$

which may be written

$$\frac{CD}{v_c^{7/3} p_c} = G, \quad . . . . . (19)$$

where  $D$  and  $G$  are functions of  $r_1$ ,  $r_2$ , and  $r_3$ . Let the limiting numerical values of  $D$  and  $G$  at the critical point, for which

$r_1=1$ ,  $r_2=1$ , and  $r_3=1$  be denoted by  $D_c$  and  $G_c$ . The equation accordingly becomes

$$\frac{CD_c}{v_c^{7/3}p_c} = G_c, \quad \dots \quad (20)$$

when referring to the critical point. Eliminating  $C$ ,  $v_c$ , and  $p_c$  from the foregoing two equations, we obtain the equation

$$\frac{D}{D_c} = \frac{G}{G_c}, \quad \dots \quad (21)$$

which contains only the variables  $r_1$ ,  $r_2$ , and  $r_3$ , and is therefore independent of the nature of the matter to which it is applied. This equation expresses the relation of corresponding states in the case when the state of matter is defined by two variables, for if two of the quantities  $r_1$ ,  $r_2$ , and  $r_3$  are taken the same for a number of substances, it follows from the equation that the value of the remaining quantity is also the same for each substance.

The relation of corresponding states can now readily be deduced for the pressure of the saturated vapour of a liquid, that is, in the case when the pressure is a function of one variable only. Suppose a number of corresponding temperatures be taken each of which refers to a liquid in contact with its saturated vapour. It follows from the result established at the beginning of this Article that the corresponding densities of the liquid and saturated vapour obey the relation of corresponding states. From equation (21) it follows then that the pressures also obey the relation of corresponding states. In conformity with the notation adopted in the case of a liquid in contact with its saturated vapour, we may therefore write  $p_1 = e_1 p_c$ , where  $p_1$  denotes the pressure of the saturated vapour, and  $p_c$  the critical pressure.

The relation of corresponding states was first deduced by van der Waals\* from his equation of state on the assumption that all the constants of the equation are determined by the

\* *Die Continuität*, Leipzig, 1881.



conditions the equation of state has to satisfy. This method of obtaining the relation will be discussed in Chapter VI. We have just seen that it can be deduced directly by the help of the thermodynamical relation (18) from the law of molecular attraction. This deduction is therefore more fundamental in character. The relation has been tested by a number of investigators, of whom Young\* should be specially mentioned. A table of his results is given in *Winckelmann's Handbuch der Physik*, 2nd ed. pp. 941-944. The substances showing the greatest deviations from the relation are those which are in a partly polymerized state. There is a good reason to believe that the deviations are caused entirely by polymerization. For in such cases we would be dealing with mixtures of substances; and it is not difficult to see that the relation of corresponding states is not likely to apply to them. In fact direct experiments have shown that the relation does not hold in the case of mixtures.

It is of importance to notice that if  $\partial u$  were not small in comparison with  $\partial U_c$ , as is assumed on the strength of certain evidence (Art. 4), the results of this Article prove that  $u-u_a$  has the same general form as  $U_c$ , or that both are functions of  $T/T_c$  and  $\rho/\rho_c$ .

11. The expression for the internal heat of evaporation given by equation (15) in Art. 6 may now be tested by the facts. The equation may be written

$$L = \{\phi_2(e_3, e_1) \cdot \rho_1^{4/3} - \phi_2(e_3, e_2) \rho_2^{4/3}\} \frac{(\Sigma e_a)^2}{m_a^{7/3}} \\ = \{A_1 \rho_1^{4/3} - A_2 \rho_2^{4/3}\} \frac{(\Sigma e_a)^2}{m_a^{7/3}} \dots \dots \dots (22)$$

by means of the equations  $\rho_1 = e_1 \rho_c$ ,  $\rho_2 = e_2 \rho_c$ , and  $T = e_3 T_c$ , given in Art. 9, and hence the quantities  $A_1$  and  $A_2$  have the same values for all substances at corresponding states. Since

\* *Phil. Mag.* (5) xxvii. 1 (1894); *Journ. Chem. Soc.* lxiii. 1191; lxvii. 1071; lxxi. 446; lxiii. 675; lxxv. 873; lxvii. 1126; lxxvii. 1145.

we also have  $\rho_2 = \frac{e_1}{e_2} \rho_1$ , the equation may also be written in the form

$$L = A_3 \frac{\rho_1^{4/3}}{m^{7/3}} (\Sigma c_a)^2, \quad . \quad . \quad . \quad . \quad . \quad . \quad (23)$$

where  $A_3$  is a corresponding state quantity, and for  $m_a$  we have written  $m$ , the molecular weight of a molecule in terms of that of a hydrogen atom.

This equation is tested in Table II.\*. The second and third columns contain the values of  $L$  and  $\rho_1$  corresponding to the temperature  $\frac{2}{3} T_c$  for a number of substances†, and the fifth column the values of  $\frac{L^{1/2} m^{7/6}}{\rho_1^{2/3}}$ . According to the above equation the latter quantity should be equal to  $A_3 \Sigma c_a$ , and thus an *atomic additive quantity*.

The values of  $A_3 c_a$  and  $c_a$  for the atoms occurring in the compounds in the Table were calculated from eight selected values of  $\frac{L^{1/2} m^{7/6}}{\rho_1^{2/3}}$  in the fifth column, and are given in the last column of the Table, the value of  $c_a$  for the hydrogen atom being put equal to unity. The values of  $A_3 \Sigma c_a$  for all the compounds were then calculated by means of the values of  $A_3 c_a$  and are placed in the sixth column of the Table. The agreement between the values in the fifth and sixth columns is very good.

The separate compartment at the end of the Table contains the names of some liquids whose molecules are known to be polymerized when in the liquid state. They do not fit in with the other liquids because, for one thing, the factor of  $\Sigma c_a$  and  $m$  expressing the extent of the polymerization has not been introduced because it is not exactly known. Besides, the critical quantities also need correction factors. For it will

\* R. D. Kleeman, *Phil. Mag.* xviii. 491 (1909).

† The values of  $L$  were interpolated from the values calculated by Mills for a number of liquids at different temperatures, and published in the *Journ. of Phys. Chem.* viii. p. 405 (1904).

TABLE II.

Name of substance.	m.	l.	$\rho_1$ .	$\frac{L^{1/2}m^{7/6}}{\rho_1^{2/3}}$ .	$A_s \Sigma c_a$ .
Benzene, $C_6H_6$ . . . . .	78	81.73	.7826	1716	1716
Pentane, $C_5H_{12}$ . . . . .	72	75.47	.6057	1784	1748
Iso-pentane, $C_5H_{12}$ . . . . .	72.1	71.09	.6048	1734	1748
Hexamethylene, $C_6H_{12}$ . . . . .	84	76.25	.7047	2128	2079
Di-isopropyl, $C_6H_{14}$ . . . . .	86	69.39	.6237	2082	2081
Hexane, $C_6H_{14}$ . . . . .	86	72.61	.6167	1941	1988
Heptane, $C_7H_{16}$ . . . . .	100	71.40	.6247	2494	2411
Octane, $C_8H_{18}$ . . . . .	114	66.05	.6299	2770	2742
Di-isobutyl, $C_8H_{18}$ . . . . .	100	66.05	.6333	2370	2412
Fluorobenzene, $C_6H_5F$ . . . . .	96.09	69.71	.9233	1936	1932
Bromobenzene, $C_6H_5Br$ . . . . .	157	48.84	1.2792	2154	2154
Iodobenzene, $C_6H_5I$ . . . . .	203.9	40.79	1.5317	2372	2372
Chlorobenzene, $C_6H_5Cl$ . . . . .	112.5	65.88	.9611	2060	2052
Stannic chloride, $SnCl_4$ . . . . .	260.8	27.11	1.9597	2192	2192
Ether, $C_4H_{10}O$ . . . . .	74	75.44	.6907	1686	1686
Carbon tetrachloride, $CCl_4$ . . . . .	142	39.87	1.4385	1766	1766
Acetic acid, $C_2H_4O_2$ . . . . .	60	86.08	.9315	1155	1202
Methyl formate, $C_2H_4O_2$ . . . . .	60	92.85	.9283	1202	1202
Propyl formate, $C_4H_8O_2$ . . . . .	88	78.35	.8304	1860	1865
Propyl acetate, $C_5H_{10}O_2$ . . . . .	102	74.30	.8046	2197	2196
Methyl acetate, $C_3H_6O_2$ . . . . .	74	89.08	.8741	1565	1533
Water, $H_2O$ . . . . .	18	455.4	.9173	660	360
Methyl alcohol, $CH_4O$ . . . . .	32	244.9	.7470	1082	692
Propyl alcohol, $C_3H_8O$ . . . . .	60	159.5	.7475	1821	1355

 $A_s c_a$ .

H = 45.5

C = 240.6

O = 269.6

F = 261.4

Cl = 381.4

Br = 483.4

Sn = 666.4

I = 703.4

 $A_c$ .

H = 1

C = 5.30

O = 5.94

F = 5.76

Cl = 8.40

Br = 10.65

Sn = 14.68

I = 15.49

appear from Art. 71 that polymerization affects the *magnitude* of the critical quantities, and therefore each quantity below the critical point, though there may be no polymerization in the critical state,

The results obtained in this Article prove that the general form assumed for the law of attraction between the molecules forming part of a liquid or gas is at least approximately correct. It will be observed that the exact form of the function ( $\phi$ ) is not determined by the investigation, and could not have been determined according to Art. 7. No other property of the function was used than that which contains the ratios  $T/T_c$  and  $z/x_c$  by virtue of which it and the quantity  $A_3$  in equation (23) have the same value for all substances at corresponding states. It should be carefully noted in this connexion, as was pointed out in Art. 7, that we can obtain trustworthy information about the law of molecular attraction from data on the internal heat of evaporation only if the law deduced contains a function which is left arbitrary in form in respect to distance of molecular separation and temperature.

12. Equation (23), when applied to substances at temperatures which are the same fraction  $\alpha$  of their critical temperatures, may be written

$$L_\alpha = \frac{b^{4/3}}{A_\alpha} \frac{\rho_\alpha^{4/3}}{m^{7/3}} (\Sigma c_\alpha)^2$$

on substituting for  $\rho_1$  from the equation  $\rho_1 = b\rho_\alpha$ , the suffix  $\alpha$  attached to a quantity indicating that it refers to the temperature  $\alpha T_c$ . We have from this equation and equation (23) that

$$L_1 = \mu_1 L_\alpha \quad . \quad . \quad . \quad . \quad . \quad . \quad (24)$$

where  $\mu_1$  is the same for all liquids at corresponding states. Therefore if  $L$  and  $L'$  are the internal heats of evaporation for two corresponding temperatures,  $L/L'$  should have approximately the same value for all liquids. This is shown in Table III. for a number of liquids corresponding to the temperatures  $\frac{2}{3}T_c$  and  $\frac{8}{9}T_c$ . From this it follows that the results of the previous Article apply to *any* corresponding temperature. The values of  $L$  used, which correspond to  $\frac{2}{3}T_c$ , are given in Table II.

TABLE III.

Name of substance.	L'.	L/L'.
Ether .....	47.33	1.593
Methyl formate .....	52.14	1.780
Carbon tetrachloride ..	25.14	1.586
Benzene .....	51.80	1.578
Stannic chloride .....	14.74	1.840
Octane .....	42.37	1.559
Propyl formate .....	49.21	1.592
Methyl acetate .....	54.67	1.629

TABLE IV.

Name of liquids.	Critical pressure in atmospheres.	Critical density.	Absolute critical temperature.	M <sub>1</sub> .	M <sub>2</sub> .
Pentane .....	33.03	.2323	470.3	120.5	25.25
Octane .....	24.64	.2327	569.2	113.2	24.56
Benzene .....	47.89	.3045	561.5	118.2	25.29
Bromobenzene.....	44.62	.4853	670.0	119.3	25.72
Iodobenzene.....	44.62	.5814	721.0	119.0	25.58
Stannic chloride ....	36.95	.7419	591.7	117.6	25.03
Carbon tetrachloride .	44.97	.5576	556.1	121.4	25.48
Carbon dioxide.....	72.9	.464	304.3	100.7	21.13

13. Equation (19) in Art. 10 on substituting for  $p_c$ ,  $v_c$ , and  $C$  from the equations

$$p = r_1 p_c, \quad v = 1/\rho = r_2 v_c, \quad \text{and} \quad C = \frac{(\Sigma c_a)^2}{m_a^{7/3}}$$

becomes \*

$$p = M_1^2 \left( \frac{\rho}{m} \right)^{7/3} (\Sigma c_a)^2, \quad . . . . . (25)$$

where  $M_1$  is the same for all substances at corresponding states. The quantity  $p^{1/2} \left( \frac{m}{p} \right)^{7/6}$  is thus additive and equal to  $M_1 \Sigma c_a$ . Table IV. contains the values of the quantity  $M_1$  for a few substances calculated from this equation by applying it to the critical point, and using the values of  $C_a$  obtained in Art. 11. It will be seen that the value of  $M_1$  is approxi-

\* R. D. Kleeman, *Phil. Mag.* xviii, 901 (1909).

mately constant, as it should be, Its mean value for a large number of substances obtained by the writer is 116.8 when the pressure is expressed in atmospheres.

14. Another equation can be deduced which is, in a sense, complementary to equation (25). According to Clapeyron's thermodynamical equation

$$L = \left( T \frac{dp}{dT} - p \right) (v_2 - v_1),$$

where  $v_2$  and  $v_1$  are the volumes of a gram of saturated vapour and liquid respectively at the temperature  $T$  and pressure  $p$ . At low temperatures  $v_1$  is small in comparison with  $v_2$ . Boyle's law may then be applied to the saturated vapour and the equation be written

$$L = \frac{RT}{m} \left( \frac{T}{p} \frac{dp}{dT} - 1 \right),$$

where  $R$  is the gas constant. Expressing  $T$  and  $p$  in terms of their critical values as before, and inserting the value of  $L$  given by equation (23) in Art. 11, we obtain

$$T = M_a^2 \left( \frac{\rho_1}{m} \right)^{4/3} (\Sigma c_a)^2,$$

where  $M_a$  is the same for all liquids at corresponding states in contact with their saturated vapours over the range of temperatures indicated. The equation can be proved to hold in general.

Let  $T_a$  and  $\rho_a$ , taken to refer to corresponding states, denote the values of  $T$  and  $\rho_1$  when the saturated vapour obeys Boyle's law, and the above equation may be written

$$T_a = M_a^2 \left( \frac{\rho_a}{m} \right)^{4/3} (\Sigma c_a)^2.$$

Next let  $T$  and  $\rho$  refer to matter in any state, and let  $T = n_5 T_a$  and  $\rho = n_6 \rho_a$ , where  $n_5$  and  $n_6$  have the same values for all substances at corresponding states. The above equation may then be written

$$T = \frac{M_a n_5}{n_6^{4/3}} \left( \frac{\rho}{m} \right)^{4/3} (\Sigma c_a)^2.$$

Therefore, since the quantities  $M_a$ ,  $n_5$ , and  $n_6$  have the same values

at corresponding states,  $M_a n_6 / n_6^{4/3}$  is a quantity of corresponding states. Therefore, in general, we may write \*

$$T = M_2^2 \left( \frac{\rho}{m} \right)^{4/3} (\Sigma c_a)^2, \dots \dots \dots (26)$$

where  $M_2$  is a quantity which is the same for all substances at corresponding states.

The above equation is tested in Table IV. for a few liquids at the critical point. The values of  $M_2$  obtained, it will be seen, are approximately constant, as should be the case. The mean value of  $M_2$  obtained from a large number of substances is 24.88.

15. From equations (25) and (26) we have

$$p = \rho \frac{RT}{m} \left( \frac{M_2}{M_1} \right)^2 = \rho \frac{RT}{M_3 m}, \dots \dots \dots (27)$$

where  $\left( \frac{M_1}{M_2} \right)^2 = M_3$ , a quantity which is the same for all substances at corresponding states. The equation resembles the well-known equation expressing the properties of a perfect gas. When applied to the critical point  $M_3$  is the same for all liquids, and this special case of the equation is known as the empirical law of Young and Thomas †. The fundamental principles underlying it are thus the law of molecular attraction given in Art. 5, and the laws of thermodynamics.

Van't Hoff in his 'Lectures on Physical Chemistry' gives the values of  $R/M_3$  for a number of substances, the mean value being 22. This gives  $M_3 = 3.7$ , which agrees well with the value  $M_3 = \frac{116.8}{24.88} = 3.66$  obtained by means of equations (25) and (26) applied to the critical point.

16. The quantity  $\frac{\rho}{m}$  which occurs in equations (27), (26), and (25) is the volume of a gram molecule of a substance, and, consequently, is proportional to the apparent molecular

\* *Loc. cit.* p. 906.

† *Phil. Mag.* (5) xxxiv. 507 (1892).

volume of a molecule. It has long been known that it is approximately an additive quantity of the atom for substances at their boiling-points at atmospheric pressure \*. It is evident, however, from what has gone before that the molecular volumes obtained for corresponding states are more likely to possess important properties, and therefore their determination under these conditions is of greater value and importance. Table V. contains the values of  $m/\rho$  for a number of substances at the critical point—the most important corresponding state—and the values of the corresponding molecular volumes calculated from the expression  $B\Sigma c_{av}$ , where  $c_{av}$  denotes the apparent volume of an atom relative to that of a hydrogen atom, and B a quantity which is the same for all substances at corresponding states, which at the critical point is a constant †. The values of  $c_{av}$  used are given at the top of the Table taking

TABLE V.

Values of $c_{av}$ for a number of atoms:—					
H = 1.	C = 2.034.	O = 2.298.	F = 2.098.		
Cl = 4.105.	Br = 5.805.	I = 7.734.	Sn = 8.59.		
Name of substance.	$\frac{m}{\rho c}$	$14.06\Sigma c_{av}$ .	Name of substance.	$\frac{m}{\rho c}$	$14.06\Sigma c_{av}$ .
Di-isopropyl . . . .	356.7	368.4	Stannic chloride . . . .	351.6	351.6
Di-isobutyl . . . . .	482.2	282.2	Benzene . . . . .	256.2	256.2
Pentane . . . . .	310.3	311.7	Carbon tetrachloride .	276.2	259.4
Octane . . . . .	490.4	482.2	Carbon dioxide . . . .	94.8	93.2
Fluorbenzene . . . .	271.4	271.4	Methyl formate . . . .	172.0	178.0
Chlorobenzene . .	307.8	299.6	Hydrochloric acid . .	61.4	73.7

the value of  $c_{av}$  for the H atom equal to unity, and the value of B equal to 14.06, corresponding to the critical point. A fair agreement between calculation and experiment is obtained. The values of  $c_{av}$  and B were obtained by first calculating the values of  $Bc_{av}$  for the H and C atoms from the two substances, di-isobutyl and benzene, and then obtaining the mean values of  $Bc_{av}$  for the other atoms from the remaining substances, a few only of which are given in the Table.

\* Proved by Kopp in 1855.

† R. D. Kleeman, *Proc. Camb. Phil. Soc.* xvii. (2) 175 (1913).



The foregoing property of the atomic volumes arises from the fact that they are additive at the absolute zero of temperature of a substance in the solid state, and that the density of a liquid in contact with its vapour obeys the relation of corresponding states. For Traube\* has shown that the gram molecular volume  $v_0$  at the absolute zero of temperature is given by

$$v_0 = 2.6 \Sigma \sqrt{a_w},$$

where  $a_w$  denotes the atomic weight of an atom in terms of that of the hydrogen atom.

The apparent volume of an atom appears to depend to a certain extent on the chemical constitution of the molecule in which it occurs, as we might expect. This property of the atomic volume has been studied for substances at their boiling-points. It appears to be much more marked in this case than when the atomic volumes refer to corresponding states.

17. Equations (26) and (27) may now be written †

$$T = (M_4)^2 \frac{(\Sigma c_a)^2}{(\Sigma c_{av})^{4/3}} \quad \dots \quad (28)$$

$$p = (M_5)^2 \frac{(\Sigma c_a)^2}{(\Sigma c_{av})^{7/3}} \quad \dots \quad (29)$$

where  $M_4$  and  $M_5$  are corresponding state quantities. These equations have a number of useful applications. Thus if the chemical formula of a substance be known the critical constants can approximately be calculated by means of the atomic constants  $c_a$  and  $c_{av}$ . The values of  $T_c$  for a few substances have been calculated in this way by means of equation (28) and are contained in Table VI., substituting for  $M_4^2$  in the equation, its mean value 17.69 corresponding to the critical point. The agreement between calculation and experiment is fair, though not quite so good as obtained in previous cases involving the quantities  $c_a$  and  $c_{av}$ , due probably to the fact

\* *Phys. Zeit.* 667 (1907).

† *Loc. cit.* p. 177.

that higher powers of  $\Sigma c_a$  and  $\Sigma c_{av}$  are involved in this case, which increases the effect of the errors in their values on the values of  $T_c$ . But still the formulæ (28) and (29) should be useful in obtaining approximately the critical values of the pressure and temperature of a substance.

TABLE VI.

Name of substance.	$\Sigma c_a$ .	$\Sigma c_{av}$ .	$T_c$ (exp.).	$T_c$ (cal.).
Chlorobenzene .....	45.2	21.31	633.0	620.7
Octane.....	60.4	34.27	569.2	588.4
Ether .....	37.2	20.43	467.4	442.7
Carbon dioxide .....	17.2	6.63	304.3	426.5
Methane .....	9.3	6.03	191.0	141.6
Hydrogen .....	2.0	2.0	38.5	28.5
Ethylene .....	14.6	8.07	282.0	290.7
Carbon tetrachloride .....	38.9	18.45	556.1	557.2
Pentane .....	38.5	22.17	470.3	427.4
Heptane .....	53.1	30.23	539.0	537.8
Di-phenyl methane .....	73.6	34.4	768.6	869.2

In chemical investigations these formulæ may be of great use, especially when the properties of a new compound are being investigated whose chemical formula can only be conjectured. Thus if by means of these formulæ the critical constants of a hypothetical substance be calculated, its pressure, and densities of the liquid and saturated vapour, can be obtained for any temperature from those of a known substance by means of the relation of corresponding states. By comparing these quantities with those found by experiment useful information for the guidance of further experiments may be obtained. As an example of the application of these principles let us calculate the critical, and related quantities, of the substance  $O_5$ , which, according to Ladenburg\*, might possibly be produced in a vacuum tube through which an electrical discharge passes. Suppose that it exists as a pure substance, that is, not as a mixture of substances whose formulæ are

\* *Ber. d. Deut. Phys. Gesell.* viii. 125 (1906).‡

of the type  $O_n$ . The critical density, temperature, and pressure in atmospheres are found in this manner to be 495, 603, and 83.3 respectively. At a temperature of 16° C. (room temperature) the substance should have a vapour pressure of 30.7 mm. of mercury and the temperature of its boiling-point should be 134° C.

Useful information may also be obtained by means of the foregoing equations about the chemical purity of a substance, that is, whether or no it consists of a mixture of two or more substances, a special case of which is partial polymerization of the molecules. For example, the values of  $c_a$  and  $c_{av}$  for an atom of copper, deduced by interpolation from the values given for a number of atoms in Arts. 11 and 16, are 9.81 and 5.18 respectively. The critical temperature of liquid copper should therefore be 190° C. Since undoubtedly it is very much higher, it follows that copper in the molten state consists in practice of molecules having the formula  $Cu_n$ , where  $n$  is probably quite large. The same conclusions can be arrived at in respect to all the other metals, and a large number of chemical compounds, such as the various salts, etc.

It will be apparent from equation (28) that the value of  $T_c$  of a substance increases with that of  $\Sigma c_a$ . Therefore the partial polymerization of a liquid should have the effect of raising its critical temperature. An important case in point is water, whose critical temperature would be 159.5° C. instead of 631° C., if the chemical formula for each molecule were  $H_2O$ . If each molecule were polymerized to the same extent, the chemical formula of a molecule would be  $8 H_2O$  according to the above equation. It appears that from surface-tension considerations water consists of molecules polymerized to different extents. The molecular weight of some of the molecules would thus be greater than that given by the foregoing expression, while for others it would be less. It may be pointed out here in passing that the determination of the extent of polymerization of a liquid from Eötvös' surface-

tension equation (Art. 71) cannot lead to very reliable results, because it is not proved that the critical temperature which occurs in the equation changes with the polymerization in such a way as to give the proper polymerization factor for the molecular weight.

Another interesting case in this connexion is the molecular weight of liquid mercury. If we take  $c_a$  and  $c_{av}$  each equal to the square root of the atomic weight of an atom of mercury, which according to Arts. 18 and 20 is approximately the case, we obtain  $604.9^\circ \text{C.}$  by means of equation (28) for the critical temperature of mercury. But it is undoubtedly much higher; from which it follows that mercury must be partially polymerized. Further evidence that this is the case will be obtained in Art. 71.

From the results of this chapter it appears that a number of very useful and important formulæ can be deduced by the help of the law of molecular attraction ( $a$ ) given in Art. 5. These formulæ were tested for the particular cases which do not involve a knowledge of the exact form of the function ( $\phi$ ) in the law except that it should obey the relation of corresponding states, and a good agreement with the facts was obtained. It may be said, therefore, that so far it has been proved that this function obeys the relation of corresponding states, and that the factor  $\Sigma c_a$  is an additive quantity in the law of molecular attraction. The nature of the constant  $c_a$  of an atom will be considered more closely in the next chapter.

## CHAPTER II.

THE ATTRACTION CONSTANTS OF THE ATOMS, THEIR CONNEXION WITH OTHER CONSTANTS, WITH CHEMICAL PROPERTIES, AND THEIR ELECTRICAL SIGNIFICANCE.

18. The constant  $c_a$ , which expresses the relative power of attraction of an atom, is of special interest in the law of molecular attraction. We should expect that it would be intimately connected with other fundamental constants. A comparison \* of the various atomic constants with the constant  $c_a$  has shown that it is proportional to the square root of the atomic weight of the atom, or that the value of  $\Sigma c_a$  of a molecule is proportional to  $\Sigma \sqrt{a_w}$ , where  $a_w$  denotes the atomic weight of an atom. This is shown by Table VII., which contains the ratio

TABLE VII.

Name of substance.	$\Sigma \sqrt{a_w}$	$\Sigma N^{2/3}$	$\frac{L^{1/2} m^{7/6}}{\rho_1^{2/3} \Sigma \sqrt{a_w}}$	$\frac{L^{1/2} m^{7/6}}{\rho_1^{2/3} \Sigma N^{2/3}}$
Ether .....	27.84	27.2	60.6	62.0
Methyl formate .....	18.92	18.6	63.4	64.6
Carbon tetrachloride ....	27.30	29.7	64.7	59.5
Fluorbenzene . . . . .	30.12	29.1	64.1	66.5
Bromobenzene .....	34.70	35.5	62.1	69.7
Iodobenzene .....	37.03	38.9	64.1	61.0
Stannic chloride .....	34.70	40.0	63.2	54.8
Di-isobutyl .....	45.68	44.4	60.5	62.2
Methyl propionate .....	29.84	29.2	62.4	63.7
Ethyl propionate .....	35.30	34.5	62.1	63.7
Ethyl formate .....	24.38	23.9	63.8	65.1

of the values of  $A_3 \Sigma c_a$  given by equation (23) to the corresponding values of  $\Sigma \sqrt{a_w}$  for a few substances at temperatures corresponding to  $\frac{2}{3} T_c$ . It will be seen that this ratio is fairly constant.

Since Glasson has shown † that the atomic weight of an

\* R. D. Kleeman, *Phil. Mag.* xix. 783 (1910).

† *Phil. Mag.* xliii. 477 (1922).

atom is approximately proportional to the  $\frac{2}{3}$  power of its atomic number  $N$  we also have that the constant  $\Sigma c_a$  of a molecule is proportional to  $\Sigma N^{2/3}$ . This is shown by the fifth column of Table VII., which gives the ratios of the values of  $A_3 \Sigma c_a$  given by equation (23) to the values of  $\Sigma N^{2/3}$ .

The constant  $c_a$  of an atom may be expressed in terms of still another fundamental quantity. Thus it was found to be proportional to the maximum chemical valency of the atom given by Traube \* or  $\Sigma c_a$  of a molecule is proportional to  $\Sigma v_a$ , where  $v_a$  denotes the maximum valency of an atom. This result is of interest on account of its bearing on the forces that operate during chemical combination. It seems to indicate that the chemical forces are the same in nature as those giving rise to the heat of evaporation of liquids.

It follows from the foregoing results that the valency of an atom is proportional to the square root of its atomic weight, a result obtained previously by Traube.

19. It is very probable that the attraction of two atoms on one another separated by a given distance is nearer being strictly proportional to the product of the square roots of their atomic weights, or to the product of the two-thirds power of their atomic numbers, than one would infer from the application of the foregoing equations to the facts, or from the constancy of the fourth and fifth columns of Table VII.

The deviations occurring when molecules are dealt with are very probably due to the atoms of a molecule not being concentrated at a point, in which case the attraction would not be accurately expressed by the product of three quantities, one a function of the distance of separation of the molecules, and each of the others equal to the sum of the attraction constants of one of the molecules. Strictly the attraction should be expressed by the sum of a number of terms each of which expresses the attraction of an atom in one of the molecules on an atom in the other molecule. Each term would therefore

\* *Phys. Z.* 667 (1909).

consist of the product of the attraction constants of the two atoms multiplied by a function of their distance of separation, which would be the same in form in each case. Since, however, these distances of separation are very probably not exactly the same, these functions will have values which would differ somewhat from each other. The attraction would therefore not be *accurately* expressed by a law of the form proposed in Art. 5 unless the atoms of a molecule are concentrated at a point.

20. The results of Art. 18 suggest that the law of molecular attraction causing internal heat of evaporation also operates during chemical combination. Now the law deduced from latent-heat data applies strictly only over distances of separation of the molecules greater than that of the molecules in the liquid state. When chemical combination takes place the atoms approach one another within a much smaller distance. It is possible, therefore, that in the latter case another law besides the one under discussion may operate which is effective only for distances of separation of the atoms which are smaller than the distance of separation of the molecules in the liquid state. It seems unlikely, however, for many reasons, that another law should exist. This cannot be tested directly, but the fact that the quantity  $c_a$  of an atom can be connected with its chemical valency is indirect evidence that the same law is operating in the two cases. Other relations of a similar nature would be further evidence, and a few more relations of this kind will therefore be pointed out in this Chapter. These relations can be discovered (as yet) by trial only, since so little of a definite nature is known about the process of chemical combination, and the resultant grouping of the atoms.

The values of the expression  $\frac{T_c}{\sum \sqrt{a_w}}$ , where  $T_c$  denotes the critical temperature, are characteristic of the purely chemical properties of substances\*. Thus they are constant for a

\* R. D. Kleeman, *Phil. Mag.* xx. 905 (1910).

substance and its substitution products. This is shown for several groups of substances (the ethane, methane, benzene, and other groups) in the upper part of Table VIII. The value of the constant, it will be seen, is, however, different for each group.

TABLE VIII.

Formula.	$\frac{T_c}{\Sigma \sqrt{a_w}}$	Formula.	$\frac{T_c}{\Sigma \sqrt{a_w}}$	Formula.	$\frac{T_c}{\Sigma \sqrt{a_w}}$	Formula.	$\frac{T_c}{\Sigma \sqrt{a_w}}$
CH <sub>3</sub> H ..	25·63	HCl ....	46·59	PCl <sub>3</sub> ....	31·94	C <sub>2</sub> H <sub>4</sub> Br <sub>2</sub> ..	48·58
CH <sub>3</sub> F ..	28·62	HBr ....	36·65	AsCl <sub>3</sub> ....	30·57	C <sub>2</sub> H <sub>4</sub> Cl <sub>2</sub> ..	59·17
CH <sub>3</sub> Cl ..	32·61	HI ....	34·53	SnCl <sub>4</sub> ....	17·05	C <sub>2</sub> H <sub>4</sub> Cl <sub>2</sub> ..	55·61
CH <sub>3</sub> Br ..	29·80	C <sub>2</sub> H <sub>5</sub> H ..	22·13	TiCl <sub>4</sub> ....	20·06	CH <sub>3</sub> H ..	20·68
CH <sub>3</sub> I ....	29·29	C <sub>2</sub> H <sub>5</sub> Cl ..	25·39	SiCl <sub>4</sub> ....	17·27	CH <sub>3</sub> F ..	18·58
C <sub>5</sub> H <sub>11</sub> Cl ..	16·11	C <sub>2</sub> H <sub>5</sub> Br ..	23·92	CCl <sub>4</sub> ....	20·37	CH <sub>3</sub> Cl ..	19·95
C <sub>5</sub> H <sub>11</sub> Br ..	15·17	C <sub>2</sub> H <sub>5</sub> I ..	23·89	SO <sub>2</sub> ....	31·36	CH <sub>3</sub> Br ..	19·3
				CO <sub>2</sub> ....	35·26	CH <sub>3</sub> I ....	19·47

Formula.	$\frac{T_c}{\Sigma \sqrt{a_w}}$	$\frac{(A_1-2O)-a(C+2H)}{a(C+2H)}$	Formula.	$\frac{T_c}{\Sigma \sqrt{a_w}}$	$\frac{(A_2-2O)-a(C+2H)}{a(C+2H)}$
C <sub>2</sub> H <sub>4</sub> O <sub>2</sub> ....	25·79	24·98	C <sub>4</sub> H <sub>8</sub> O <sub>2</sub> ....	20·47	20·14
C <sub>6</sub> H <sub>10</sub> O <sub>2</sub> ....	15·51	16·45	C <sub>2</sub> H <sub>4</sub> O <sub>4</sub> ....	31·42	31·22
C <sub>7</sub> H <sub>14</sub> O <sub>2</sub> ..	12·71	11·43	C <sub>3</sub> H <sub>6</sub> O <sub>2</sub> ....	25·14	25·68

Formula.	$\frac{T_c}{\Sigma \sqrt{a_w}}$	$\frac{(A_2-N-3H)-a(C+2H)}{a(C+2H)}$
C <sub>2</sub> H <sub>7</sub> N .....	25·48	27·25
CH <sub>5</sub> N .....	35·05	34·26
CHN .....	21·21	20·24

If  $\phi$  (H, C, N, O, ...) denote the general chemical formula for a chemical group of substances, the quantities  $A_1$ , H, C, N, ..., in the equation

$$A_1 - \phi(H, C, N, O, \dots) = \frac{T_c}{\Sigma \sqrt{a_w}}$$

will have the same values for all substances belonging to the group. This is shown for some esters, acids, and amines in lower part of Table VIII. The equation for the esters is

$$A_1 - \{2O + \alpha(C+2H)\} = (A_1 - 2O) - \alpha(C+2H) = \frac{T_c}{\Sigma \sqrt{a_w}} \dots (30)$$

where  $\alpha$  is an integer. The values of  $(A_1 - 2O)$  and  $(C+2H)$



were found from this equation applied to the facts by the method of least squares to be equal to 29 and 2.51 respectively.

The values of  $\frac{T_c}{\sum \sqrt{a_w}}$  were then calculated from the foregoing equation by means of these values and found to agree well with those obtained directly. The equation for the acids in the Table is the same as that for the esters, but the values of  $(A_1 - 2O)$  and  $(C + 2H)$  are now 42.3 and 5.54 respectively. The equation for the primary and secondary amines is

$$(A_2 - N - 3H) - \alpha(C + 2H) = \frac{T_c}{\sum \sqrt{a_w}} \quad (31)$$

In the case of the primary amines the values of  $(A_2 - N - 3H)$  and  $(C + 2H)$  are 41.27 and 7.01 respectively, while in the case of the secondary amines the values are 29.05 and 2.62. Other relations of the same nature will be found in the paper cited.

21. The quantity  $\sum \sqrt{a_w}$  can also be connected with the heats of combustion of compounds. Thus in the case of the hydrocarbons  $Q/\sum \sqrt{a_w}$  is a constant whose mean value is 29.5, where  $Q$  denotes the heat of combustion in kilogram calories per gram molecule, and  $\sum \sqrt{a_w}$  the sum of the square roots of the atomic weights of the hydrogen and carbon atoms in a molecule. This is shown for a few hydrocarbons in Table IX.

TABLE IX.

Name of substance.	Q.	$\frac{Q}{\sum \sqrt{a_w}}$ .
Methane, $CH_4$ .....	213.5	28.63
Ethane, $C_2H_6$ .....	372.3	28.80
Acetylene, $C_2H_2$ .....	313.8	35.18
Propane, $C_3H_8$ .....	528.4	28.74
Butane, $C_4H_{10}$ .....	687.2	29.19
Hexane, $C_6H_{14}$ .....	991.2	28.52
Heptane, $C_7H_{16}$ .....	1152.3	28.65
Toluene, $C_7H_8$ .....	933.8	28.92
Diphenylmethane, $C_{18}H_{12}$ .....	1659.9	29.12
Tryphenylmethane, $C_{18}H_{14}$ ....	2387.3	29.20
Triphenylbenzene, $C_{24}H_{18}$ .....	2938.3	29.02
Tetraphenylmethane, $C_{26}H_{20}$ ..	3104.1	29.15

This property of the hydrogen and carbon atoms persists in all compounds, and is isolated by subtracting algebraically quantities from the heats of combustion which represent the effect of the other atoms \*. Thus, for example, in all compounds containing atoms of H, C, and O, we have

$$\frac{Q - n \cdot 50.7}{\sum \sqrt{a_w}} = 29.5, \dots \dots \dots (32)$$

where  $n$  denotes the number of oxygen atoms in a molecule, and 50.7 is a quantity which may be said to represent the effect of an oxygen atom on the heat of combustion.

Equations resembling the above equation exist for other kinds of compounds. But the effect of an atom other than one of H, C, or O is not always the same in every compound. It is usually the same for a chemical group of substances, but exceptions occasionally occur. An account of these divergencies, which probably have an important chemical significance, will be found in the paper cited, in which all the available data have been investigated.

22. The attraction constants of the atoms of a molecule should also be connected with the internal specific heat  $c_i$  of a gram molecule of molecules in the gaseous state at constant volume, since a change in temperature is very probably attended by a change in the configuration of the atoms of each molecule under the action of their forces of attraction and repulsion. This specific heat is given by

$$c_i = c_v - \frac{3}{2}R, \dots \dots \dots (33)$$

where  $c_v$  denotes the specific heat at constant volume, and  $3/2R$  the increase in the kinetic energy of molecular motion of translation per unit increase in temperature. It was found † that

$$\ln c_i = h_1 \sum N^{2/3} = h_2 \sum \sqrt{a_w} \dots \dots \dots (34)$$

where the values of  $c_i$  refer to the temperature 0° C., and  $h_1$

\* R. D. Kleeman, *Proc. Camb. Phil. Soc.* xvi. (4) 299 (1911).

† R. D. Kleeman, *J. Frank. Inst.* 479, Oct. 1923.

and  $h_2$  are approximately constants. This is shown by Table X., which contains the values of  $c_v$ ,  $c_i$  for a number of gases, and the values of  $h_1$  and  $h_2$  given by the foregoing equation.

TABLE X.

Name of gas.	$c_v$ .	$c_i$ .	$\frac{\ln c_i}{\Sigma \sqrt{a_w}}$ .	$\frac{\ln c_i}{\Sigma N^{2/3}}$ .
Carbon disulphide, $\text{CS}_2$ . . . . .	8.01	5.07	475	441
Chloroform, $\text{CHCl}_3$ . . . . .	14.05	11.11	468	433
Ethyl bromide, $\text{C}_2\text{H}_5\text{Br}$ . . . . .	12.72	9.78	452	442
Acetone, $\text{C}_3\text{H}_6\text{O}$ . . . . .	15.30	12.36	536	548
Benzene, $\text{C}_6\text{H}_6$ . . . . .	15.48	12.54	410	425
Ethyl acetate, $\text{C}_4\text{H}_8\text{O}_2$ . . . . .	21.00	18.06	424	430
Ether, $\text{C}_4\text{H}_{10}\text{O}$ . . . . .	25.50	22.56	486	497

It is very likely that the specific heat  $c_i$  of substances should be compared at corresponding temperatures, in parallel with so many properties of substances. Equation (34) would accordingly assume the form

$$\ln c_i = \psi\left(\frac{T}{\bar{T}}\right), \Sigma N^{2/3}, \quad . \quad . \quad . \quad . \quad . \quad (35)$$

where the function  $\psi$  is evidently not sensitive to variations of  $T$ , and is the same for all substances.

23. The heat of formation  $H$  of a gram molecule of a compound in the gaseous state is connected with its specific heat  $c_v$  at constant volume and the specific heats  $c_{va}$  and  $c_{ve}$  of the molecular constituents of a molecule by the well-known equation

$$\left(\frac{\partial H}{\partial T}\right)_v = n_a c_{va} + n_e c_{ve} - c_v, \quad . \quad . \quad . \quad . \quad . \quad (36)$$

where  $n_a$  denotes the number of molecules  $a$  and  $n_e$  the number of molecules  $e$  forming part of a molecule of the substance. On substituting from equations (33) and (35) and integrating this equation a relation between  $H$  and the attraction constants of the atoms is obtained.

24. The atomic forces may be completely explained \* by

\* *Loc. cit.*

means of electrical attraction and repulsion. It may be regarded as definitely established that the atom consists of a positive nucleus around which are arranged a number of electrons of equal total charge. Two atoms or molecules would therefore, on account of the asymmetrical distribution of electricity, exert electrical forces upon each other. And if the electrons in an atom are in motion magnetic forces would also come into play, but these would probably be much smaller than the electrical forces. Let us represent these forces as being due to an electrical doublet (constant at constant temperature and volume) of moment  $M$  associated with each atom or molecule. It does not follow, however, it should be carefully noted that an atom or molecule actually possesses a *definite uniaxial* electrical moment, though two atoms or molecules probably in most cases affect each other as if they consisted of electrical doublets. The moments of these doublets\* would depend on their distance of separation during their motion in a liquid or gas, since they would act inductively on each other, and besides vary their orientation with respect to each other, etc. The mean of all these effects in a liquid or gas will be represented by the constant moment  $M$ .

A number of such doublets in space would tend to set themselves with their axes in positions so that the potential energy would be a minimum. Attraction would accordingly tend to be the outstanding force. It can easily be shown that this can be realized.

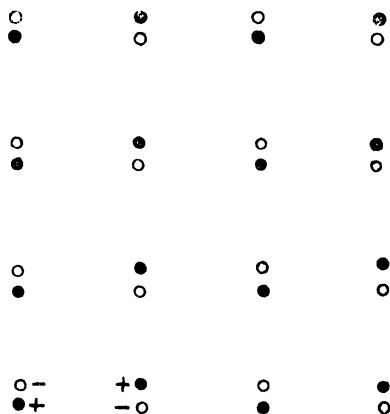
Thus a number of doublets lying with their axes on a straight line with opposite charges facing one another, as shown in fig. 3, would attract each other. These doublets would evidently attract the doublets in another similar row parallel to the foregoing, whose positive charges face in the opposite direction. Thus attraction would be the force in all directions under these conditions. If the doublets were now uniformly rotated round axes situated at right angles to their length, in

\* The resultant of a number of diffusely arranged doublets.

such a way that the axes of the doublets remain parallel to each other, attraction would still be the outstanding force in all directions. The system would, however, not now possess any electric polarity.

In a liquid or gaseous substance the molecular collisions would interfere with the tendency of the doublets to set themselves so that attraction is the outstanding force, in suddenly changing the directions of the axes of the doublets of each pair of colliding atoms or molecules. Any direction of an axis of a doublet in space would be equally probable, since a gas or liquid as a whole has no electric polarity. But an association or connexion would exist between the various directions of

Fig. 3.



the axes of the doublets at any instant in conformity with having the potential energy a minimum, so that attraction would tend to be the outstanding force. Thus two molecules which are closer to each other than to other molecules would exert a torque upon each other, tending to rotate their doublets so as to increase the attraction between them. This would go on till the molecules undergo a collision, which would arbitrarily give the axes of the doublets new directions in space, and if no collision occurs the molecules would move out of each other's influence. Thus the axis of a molecular doublet

would be oftener parallel to that of another doublet than at right angles to it, and hence attraction would be the outstanding force.

It may happen, of course, that for certain densities and temperatures of the substance the effect of molecular collision on the orientation of the electrical doublets may be such that repulsion is produced between the atoms instead of attraction. But this repulsion, since the potential energy is to be a minimum, would be as small as possible.

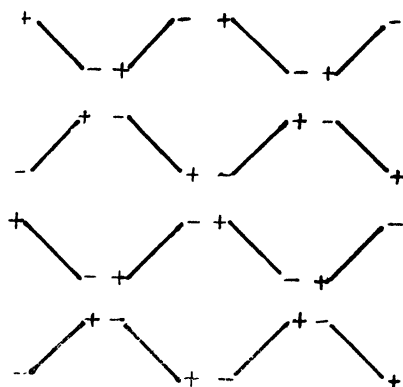
Debye supposes\* that the attraction between atoms and molecules arises through a change in the distances of separation of the charges of the doublets of two approaching atoms or molecules in such a manner that attraction is the outstanding force. Now such contractions and expansions probably occur, as we have already seen, but it is not necessary to bring them in to explain molecular attraction. Attraction would be the outstanding force according to the preceding investigation, even if the doublets remain unchanged under each other's action.

25. The absolute value of the representative electrical moment  $M$  of a molecule may be determined on considering substances at or near the absolute zero of temperature, at which the disturbing effect of molecular collision will be negligible. We may then suppose that the molecules of a substance are situated in their mean positions and the axes of the doublets pointing in directions giving a minimum of potential energy in conformity with having equal and opposite forces acting on each molecule when in equilibrium. The average positions of the molecules in space correspond, according to Art. 3, to the points of intersection of three sets of parallel and equidistant planes at right angles to each other. Suppose that the axes of the doublets lie on the diagonals of the cubes formed by the foregoing planes of reference in such a way that a projection of the doublets

\* *Phys. Z.* **xxi.** 178 (1920); **xxii.** 303 (1921).

on to each of the planes on which their centres lie gives an arrangement as shown in fig. 4, in which the projected axes of the doublets are at right angles with opposite electrical charges facing each other. The doublets thus actually lie on three systems of parallel and equidistant planes at right angles to each other, each of which makes an angle of  $45^\circ$  with one of the planes of reference. The force acting on a doublet in one direction along an axis formed by the intersection of two of the planes of reference is evidently equal to the force acting in the opposite direction, and each force is an attraction.

Fig. 4.



The force is the same along each of three rectangular axes, each of which corresponds to a row of molecules. Now the attraction between two doublets of moment  $M$  lying on a plane, and making angles  $\theta_1$  and  $\theta_2$  with the line of length  $z$  joining their centre, is

$$-\frac{3M^2}{z^4} (2 \cos \theta_1 \cos \theta_2 - \sin \theta_1 \sin \theta_2).$$

The attraction between two doublets whose centres are separated by a distance  $z$  and are situated on a line formed by the

intersection of the foregoing planes of reference, is therefore given by

$$4.5 \frac{M^2}{z^4},$$

since the doublets lie on a plane and are inclined at an angle of  $45^\circ$  to the line joining their centres. The attraction between two doublets not lying in the same row will evidently be less than that given by the foregoing expression. For our purpose it is necessary to obtain the average law applying to any pair of doublets. An approximation to this law is obtained from the following considerations:—

Two doublets lying on the same straight line with opposite charges facing each other exert the attraction

$$\frac{6M^2}{z^4}$$

upon each other, while if the axes are parallel and opposite charges face each other, the attraction is

$$\frac{3M^2}{z^4}.$$

Now suppose that the doublets are placed parallel to each other and parallel to one of the axes formed by the intersection of the three systems of intersecting planes defining the position of the molecules in space. The charges of the doublets are arranged so that opposite charges face each other along each of the three rectangular axes formed by the planes. The attraction along one of the axes is then given by the former of the foregoing expressions, and the attraction along the two remaining axes by the latter expression. We may therefore suppose that the average attraction in any direction under symmetrical conditions is apparently given by

$$\frac{6 + 3 \times 2}{3} \frac{M^2}{z^4} = \frac{4M^2}{z^4}.$$

The attraction given by this expression is a little less than



that given by the preceding investigation, which we have seen is larger than the average attraction. Now it is evident from the foregoing investigation that the average attraction is larger than  $3 M^2 z^4$ . It must therefore lie between  $3 M^2/z^4$  and  $4.5 M^2/z^4$ . We will therefore take  $4 M^2/z^4$  to represent approximately the average attraction. This average law will be taken to apply to any density of the substance. An expression for  $M$  corresponding to this law may now be deduced.

If the attraction between two molecules, or atoms, is given by

$$\frac{K}{z^5},$$

where  $z$  denotes their distance of separation and  $K$  a constant, the internal heat of evaporation  $L$  in ergs per gram is given by\*

$$L = 1.58 \frac{\rho_1^{4/3}}{m^{7/3}} K, \quad . \quad . \quad . \quad . \quad . \quad . \quad (37)$$

if the vapour obeys the gas laws, where  $\rho_1$  denotes the density of the substance, and  $m_a$  the absolute mass of a molecule. This expression for  $L$  involves a factor obtained by the integration of

$$\int \frac{1}{z^4} \cdot dz,$$

which gives

$$\frac{1}{4z^3} = \frac{1}{4} \left( \frac{\rho_1}{m_a} \right)^{4/3},$$

where

$$\left( \frac{m_a}{\rho_1} \right)^{1/3} = z,$$

the distance of separation of the molecules. The latent-heat expression corresponding to the law of attraction

$$\frac{K}{z^5}$$

\* R. D. Kleeman, *Proc. Camb. Phil. Soc.* xvi. (7) 583 (1912).

is therefore obtained from the foregoing expression on multiplying it by

$$\frac{1}{s-1} \left( \frac{\rho_1}{m_a} \right)^{\frac{s-1}{3}} / \frac{1}{4} \left( \frac{\rho_1}{m_a} \right)^{4/3},$$

which gives

$$L = \frac{6.32}{s-1} \frac{\rho_1^{\frac{s-1}{3}}}{m_a^{\frac{s+2}{3}}} K. \quad . \quad . \quad . \quad . \quad . \quad (38)$$

In the special case under consideration  $s=4$  and  $K=4 M_0^2$ , which gives the foregoing equation the form

$$L_0 = 8.42 \frac{\rho_0}{m_a^2} M_0^2. \quad . \quad . \quad . \quad . \quad . \quad (39)$$

where  $L_0$  denotes the internal heat of evaporation,  $M_0$  the representative moment, and  $\rho_0$  the density at the absolute zero of temperature. The values of  $L_0$  may be obtained by extrapolation, using the latent heat equation  $L = (\rho_1^2 - \rho_2^2) k_3$  given in Art. 61, which is probably the best for this purpose, and from which it can be deduced that

$$L_0 = \left( \frac{\rho_0}{\rho_1} \right)^2 L, \quad . \quad . \quad . \quad . \quad . \quad (40)$$

where  $L$  denotes a known value of the latent heat, and corresponds to a known value  $\rho_1$  of the density. The value of  $L_0$ , it should be noticed, corresponds to the general nature of the molecules remaining unchanged down to the absolute zero, which need not actually be the case in practice. Table XI. gives the values of the moments of a few molecules calculated by the writer\* in this way, and the values of  $L_0$ ,  $L$ , and  $\rho_1$  used. It was found that the values of  $M_0/\Sigma N^{2/3}$  are approximately constant, as is shown in the Table, their mean value being  $10^{-19}$ . We thus have that

$$M_0 = 10^{-19} \Sigma N^{2/3}. \quad . \quad . \quad . \quad . \quad . \quad (41)$$

or the moment of a molecule at the absolute zero of tempera-

\* R. D. Kleeman, *J. Frank. Inst.* 479, Oct. 1923. The charge is expressed in e.s.u., and  $\rho_0$  is obtained from a paper by Traube, *Phys. Zeit.*, Oct. 1909, p. 667.

ture is an additive quantity of the atoms proportional to the attraction constant (Art. 18).

26. The distance  $x$  between the electrical charges of magnitude  $e$  of the representative doublet of an atom may now be calculated by means of the equation

$$Nex = M_0 = 10^{-10} N^{2/3} \quad . \quad . \quad . \quad . \quad . \quad (42)$$

On writing  $e = 4.77 \times 10^{-10}$  e.s.u. (Millikan's value) we obtain

$$x = 2.09 \times 10^{-16} N^{-1/3} \text{ cm.} \quad . \quad . \quad . \quad . \quad . \quad (43)$$

Thus the distance  $x$  is less than the molecular diameter, as should be the case, and decreases with increase of atomic weight. The reason for the decrease is, obviously, that the

TABLE XI.

Substance.	T.	$\rho_{11}$	L in cal.	$L_0$ in cal.	$M_0 10^{18}$ .	$\Sigma N^{2/3}$ .	$\frac{M_0 10^{18}}{\Sigma N^{2/3}}$ .
Iodobenzene . . . . .	303	1.8149	53.75	83.9	3.51	38.9	9.03
Chlorobenzene . . . . .	273	1.1278	82.90	132.2	3.08	31.4	9.77
Fluorobenzene . . . . .	273	1.0465	81.74	138.1	2.71	29.1	9.42
Bromobenzene . . . . .	303	1.4815	64.84	107.6	3.33	35.5	9.40
Carbon tetrachloride .	273	1.6327	48.35	81.12	2.70	29.7	9.10
Benzene . . . . .	273	.9001	100.16	170.6	2.66	25.8	10.31
Ethyl ether . . . . .	273	.7362	86.16	165.1	2.67	27.2	9.80
Acetone . . . . .	273	.8186	131.82	223.2	2.35	20.9	11.24
Sulphur dioxide . . . .	263	1.460	86.56	173.0	1.66	14.36	11.55
Carbon dioxide . . . . .	243	1.045	65.34	177.8	1.27	11.3	11.20

greater the number of electrons in an atom, the more symmetrically they may be grouped, and are likely to be grouped, about the central nucleus.

27. At temperatures above the absolute zero the effectiveness of the molecular moments  $M$  in exerting attraction upon each other is decreased by molecular collision. This effect cannot be calculated, especially since  $M$  does not represent an actual moment, but the sum total of a number of complicated

effects equivalent to a moment. But we may represent the effectiveness of these molecular moments modified by collision by a number of moments stationary in space, the axes of the moments assuming the positions indicated in Art. 24, which correspond to the potential energy being a minimum. At the absolute zero of temperature these moments become identical.

Equation (39) may then be transformed to apply to a substance at temperatures above the absolute zero, and accordingly be written

$$L_c = 8.42 \frac{\rho_1}{m^{\frac{1}{2}}} m_0^2, \dots \dots \dots (44)$$

where  $m_0$  denotes the stationary electrical moment that would give rise to the heat of evaporation  $L_c$  into a vacuum, and is the moment  $M$  modified in effectiveness by its rotations, etc., caused by molecular collisions. From this equation and equation (39) we have

$$\frac{M_0}{m_0} = \sqrt{\frac{I_0 \rho_1}{L_c \rho_0}} = \sqrt{\frac{I_0 \rho_1 \rho_2}{\rho_0 (T \frac{d\rho}{dT} - \rho)}} \dots \dots \dots (45)$$

by the help of equation (6), where  $\rho_2$  denotes the density of the saturated vapour at the absolute temperature  $T$  and pressure  $p$ . This equation holds for a liquid up to the critical point. It does not depend, it should be noticed, on the magnitude of the numerical factor in the law  $\frac{4M^2}{z^4}$ , on which equation (39) is based.

It is evident from the equation that the ratio  $M_0/m_0$  is the same for all substances at corresponding states. Hence  $m_0$  is also an additive quantity of the atoms of a molecule proportional to  $\Sigma N^{2/3}$ . It will be of interest to determine the ratio for the critical point. In the case of ether we have  $L_0=165$  cal.,  $\rho_0=1.02$ ,  $\rho_c=.2604$ ,  $p_c=26.28$  atmos., and  $L_c=6.5$  cal. obtained for the critical point by the help of equations (9)

and (6). Accordingly we obtain

$$\frac{M_0}{m_0} = 1.4. \quad . \quad . \quad . \quad . \quad . \quad . \quad (46)$$

The value of the ratio being greater than unity indicates the existence of the disturbing effect of molecular collision on the interaction of the molecular doublets, which would vary with the temperature and density. It appears also from the result that at ordinary temperatures the stationary representative molecular moment  $m_0$  of a molecule in a liquid at room-temperature is about 20 per cent. less than the representative moving moment  $M$ , which is probably little less in magnitude than the moment  $M_0$  at the absolute zero.

28. Equation (44) may be given a more general form. On multiplying the well-known thermodynamical equation

$$\left(\frac{\partial U}{\partial v}\right)_T = T \frac{\partial p}{\partial T} - p \quad . \quad . \quad . \quad . \quad . \quad (47)$$

by  $\partial v$ , where  $U$  denotes the internal energy, and integrating it between the limits  $v$  and  $\infty$ , we obtain

$$L_c = U_c = \int_v^\infty \left\{ T \left(\frac{\partial p}{\partial T}\right)_v - p \right\} \partial v, \quad . \quad . \quad . \quad (48)$$

where  $U_c$  has the usual meaning. Now, according to equation (44), we may write  $8.42 \frac{\rho_1}{m_a^2} m_0^2$  for  $L_c$ , and hence

$$m_0 = \frac{m_a}{\sqrt{8.42 \rho_1}} \sqrt{\int_v^\infty \left\{ T \left(\frac{\partial p}{\partial T}\right)_v - p \right\} \partial v}. \quad . \quad . \quad . \quad (49)$$

This equation may be applied to matter in any state to calculate the representative stationary moment  $m_0$ .

29. Neither the moment  $M$  nor  $m_0$  need have any definite relation to the moment a molecule appears to possess under the influence of a parallel external electric field, for the fields to which the molecules subject each other are far from being

parallel. Besides, on account of the motion of the molecules the angle between the lines of force in which a molecule is situated is continually changing. Now it will not be difficult to see that the apparent electrical moment of a molecule depends considerably on the nature of the field in which it is placed. Induction effects will also exist depending on the nature of the field. A molecule in a liquid or gas whose moment is small, or zero, in an external electric field may therefore have normal representative moments of the kind  $M$  and  $m_0$ . This would, for example, be the case if electrically a molecule may be represented by two equal and parallel doublets facing in opposite directions. Such a molecule would not possess a moment in an external parallel electric field, but two such molecules would exert forces on each other on close approach. A case in point is methane. It has been found that a molecule of methane possesses little or no moment in a parallel external field. But the representative stationary moment  $m_0$  obtained on the supposition that the electrical forces are electrical in nature is found to be normal.

But in spite of the divergencies in the nature and magnitude of these moments, it may be stated that, if the average moment of sets of different molecules corresponding to a parallel field is of the same order of magnitude as the average representative moment  $M$  or  $m_0$ , this would be evidence that the molecular forces are entirely electrical in nature. Such evidence will now be considered.

The moment of a molecule in an external electric field is usually divided into two, viz., a permanent and an induced moment, the permanent moment being usually the larger of the two. The permanent moment  $M_p$  may be determined from measurements of the inductivity  $K$  and other quantities. The relation

$$K = S_1 + \frac{S_2}{T} \dots \dots \dots (50)$$

applying to gases at constant volume was first formulated by

Debye\*, where  $S_1$  and  $S_2$  are constants. For liquids the expression developed was

$$\frac{K-1}{K+2} = S_3 + \frac{S_2}{T}, \quad . . . . . (51)$$

where  $S_3$  and  $S_2$  are constants for a given liquid,  $S_2$  being connected with the electric moment  $M_p$  by the equation

$$M_p = \sqrt{\frac{3}{4\pi}} \sqrt{\frac{S_2 R}{N_0 N_c}}, \quad . . . . . (52)$$

where  $N_c$  denotes the number of molecules per  $\text{cm}^3$  and  $N_0$  the number of molecules per gram molecule. The deduction of these equations depends on certain assumptions and approximations. More general equations have been developed by Gans and Isnardi†. Smyth‡ has modified the equations of Gans, enabling him to calculate  $M_p$  for a substance in the liquid or gaseous state from the indices of refraction at two

TABLE XII.

Liquid Ether.

$t^\circ\text{C.}$	K.	$\rho$ .	$M_p 10^{18}$ .
-100	8.143	.8410	1.373
- 80	7.049	.8205	1.373
- 54	6.33	.7930	1.409
0	4.683	.7359	1.410
18	4.36	.7150	1.420
160	2.41	.4927	1.420

Gaseous Ether.

100	1.00516	.00242	1.513
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different wave-lengths, the density of the substance under which the indices are measured, a value of the dielectric constant and the temperature and density at which it is measured, the molecular diameter, the molecular weight, and

\* *Phys. Zeit.* xiii. 97 (1912).

† R. Gans, *Ann. d. Phys.* lxiv. 481 (1921); H. Isnardi and R. Gans, *Phys. Zeit.* xxii. 230 (1921); H. Isnardi, *Zeits. f. Phys.* ix. 152 (1922).

‡ C. P. Smyth, *Phil. Mag.* xlv. 850 (1923).

certain universal constants. Table XII. gives some calculation carried out by Smyth with ether. It will be seen that the values of  $M_p$  obtained from the liquid state vary little with the temperature as we would expect, and the value obtained from the gaseous state is practically the same as that obtained from the liquid state at the same temperature. From this we conclude that the results obtained represent at least approximately the facts. The values obtained by Gans and Isnardi, it may be mentioned, are of the same order of magnitude.

In general it is found that the values of  $M_p$  obtained from values of the inductivity of a number of substances by various investigators using somewhat different formulæ are of the same order of magnitude as the values obtained in Arts. 25 and 27 for  $M_0$  and  $m$  from latent heat considerations. This is fair evidence that the molecular forces giving rise to the internal heat of evaporation, surface tension, etc., are electrical in nature.

30. The result that a molecule possesses a representative electrical doublet whose moment is proportional to  $\Sigma\sqrt{a_w}$  or  $\Sigma N^{2/3}$  (Arts. 25 and 18) receives a striking confirmation from the range of the  $\alpha$  particle of radium in different gases\*. An  $\alpha$  particle, as is well known, carries a positive charge equal to  $2e$ , which consists of the positive nucleus of a helium atom. In passing through a gas it would spend its kinetic energy in part, if not altogether, on the molecules of the gas, if they behave as electrical doublets, through the forces of attraction and repulsion called into play. On account of the high velocity of the  $\alpha$  particle we may consider the molecules approximately at rest during its passage. Since each direction of the axis of an atomic doublet in space is equally probable, the *average* force between the  $\alpha$  particle and a molecule separated by a distance  $z$ , considering a large number

\* R. D. Kleeman, *Phil. Mag.* p. 804 (May 1910).



of cases of repulsion or attraction, is

$$K_a \frac{M}{z^n},$$

where  $K_a$  denotes an absolute constant, whose sign indicates the nature of the force called into play. Now Maxwell has shown\* that a particle of mass  $m_1$  and velocity  $V$  in passing through a gas of molecular concentration  $N_c$  and molecular mass  $m_2$  expends its energy, when the law of force corresponds to  $K/z^n$ , at a rate along its path given by

$$\frac{dV}{dz} = - \frac{m_2}{m_1 + m_2} \left\{ \frac{K(m_1 + m_2)}{m_1 m_2} \right\}^{\frac{2}{n-1}} N_c A_c V^{\frac{n-5}{n-1}}, \quad \dots \quad (53)$$

where  $A_c$  denotes a constant whose sign is the same as that of  $K_a$ . In the particular case under consideration  $n=3$ ,  $K=K_a M$ , and hence

$$\frac{dV}{dz} = - \frac{K_a M N_c A_c V^{-1}}{m_1}. \quad \dots \quad (54)$$

From this equation it can easily be deduced by integration that

$$\frac{1}{2} m_1 (V_1^2 - V_2^2) = K_a N_c A_c M (z_2 - z_1), \quad \dots \quad (55)$$

where  $z_2 - z_1$  denotes the range of the  $a$  particle corresponding to the change in kinetic energy expressed by the left-hand side of the equation. Thus the range for a constant molecular concentration  $N_c$  is inversely proportional to the moment  $M$  of a molecule of the gas †, or inversely proportional to the sum  $\Sigma \sqrt{a_w}$  of the square roots of the atomic weights of a molecule, according to Art. 25, provided the  $a$  particle spends its energy mainly as described. This is the result found previously by experiment by Bragg and the writer ‡, who measured the range of the  $a$  particle in a large number of gases and found their range inversely proportional to  $\Sigma \sqrt{a_w}$ . The writer § has

\* Maxwell's *Collected Papers*, ii. 36.

† R. D. Kleeman, *Phys. Rev.* xviii. 303 (1921).

‡ *Phil. Mag.* x. 318 (1905).

§ *Proc. Roy. Soc. A*, lxxxiv. 16 (1910).

shown that it also holds for the range of slow-moving electrons.

Some of the energy of the  $\alpha$  particle will, of course, be expended in ionizing molecules, but since the particle passes thousands of molecules to every one it ionizes, this energy is likely to be small in comparison with that which it spends otherwise. But even that energy would be spent approximately according to the above law. For the ionization produced by an  $\alpha$  particle has been shown to be approximately proportional to the molecular volume, and this volume is proportional to  $\Sigma\sqrt{a_w}$  according to Art. 16. This result indicates that the chance of an  $\alpha$  particle to ionize a molecule is proportional to the force it exerts upon it, as we might expect.

31. The molecules in a liquid or gas not only undergo motions of translation, but vibrations as well, under the action of the electrical forces they exert upon each other, as will now be shown. An atomic electrical doublet sets itself parallel to the electrical field in which it is placed, and if deflected from its position of equilibrium by a small angle and then released will execute harmonic vibrations. The period  $\tau$  of these vibrations is given by

$$\tau = 2\pi\sqrt{\frac{I}{MH}}, \quad . . . . . (56)$$

where  $I$  denotes the moment of inertia of the electrons of the atom about its axis of vibrations which coincides with the nucleus,  $M$  denotes the electrical moment of the atom, and  $H$  the electrical field in which it is placed. The value of  $M$  as a first approximation may be taken to be given by equation (41), and the value of  $I$  by

$$I = \frac{Nx^{21.65} \times 10^{-24}}{1800}, \quad . . . . . (57)$$

where  $N$  denotes the atomic number of the atom, or the number of electrons it contains in the electronic shell,

$x$  the radius of gyration of the electronic mass, and  $\frac{1.65 \times 10^{-24}}{1800}$  the mass of an electron. Equation (56) may therefore be written

$$\tau = 10^{-4} x N^{1/6} H^{-1/2}. \quad . . . . . (58)$$

Besides, we have the equation

$$\lambda = \tau c, \quad . . . . . (59)$$

where  $\lambda$  denotes the wave-length of the radiation, and  $c$  the velocity of light. The quantity  $x$  may be taken less than the radius of the molecule. The field  $H$  is approximately given by  $Ma/r^3$ , where  $a$  denotes a factor of the order unity, and  $r$  the distance between two molecules which, of course, is continually changing. It can then easily be shown that:

(a) A continuous radiation is omitted by the substance whose wave-length varies from the longest heat waves to the shortest waves in the ultra-violet region.

(b) An increase in temperature would increase the proportion of high-frequency to low-frequency radiation.

(c) The energy of the radiation per atom or molecule would increase with the density of the substance.

(d) The nature of the radiation would depend on the density of the substance and its nature.

(e) An electric or magnetic field applied to the substance would have the effect of shifting the period of vibration up the spectrum, give rise to an asymmetrical emissivity and absorbing power of the substance in respect to the orientation of the field, and to a certain extent have a polarizing effect on the radiations emitted. But these effects could be detected experimentally only under the application of enormous fields.

Thus the electric polarization of molecules not only gives rise to the forces the molecules exert upon each other, but also contributes to the general radiation of a body.

The radiation we would expect to take place subject to the quantum conditions\*, so that when the energy of the

\* R. D. Kleeman, *Z. f. Phys.* lxxviii, 286 (1931).

vibrating system falls from  $\xi_n$  to  $\xi_m$  in passing from the state  $n$  to the state  $m$  we have

$$\xi_n - \xi_m = h\nu, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (60)$$

where  $\nu$  denotes the frequency of the radiation and  $h$  Planck's constant. Hence when the amplitude of the vibrating doublet changes from  $A_1$  to  $A_2$  we have

$$\frac{2N \cdot 1.65 \times 10^{-24} \pi^2}{1800} (A_1^2 - A_2^2) = h\nu^{-1}. \quad . \quad . \quad . \quad (61)$$

The oscillating doublets accordingly represent a species of Planckian resonators\*.

In this chapter it was shown that the attraction constant of a molecule is connected with some of its well-known fundamental constants, and that it represents the effect of the electrical charges in the molecule. In the next chapter some (approximate) properties of the function ( $\phi$ ) in the law of molecular attraction will receive consideration.

\* The atom or molecule may, of course, radiate in many other ways. It is desired here only to call attention to the radiating possibilities connected with quantities related to the molecular forces.

## CHAPTER III.

THE INTRINSIC PRESSURE, SPECIFIC HEAT, AND THE JOULE THOMSON EFFECT IN CONNEXION WITH MOLECULAR FORCES, AND THE TEMPERATURE VARIATIONS OF THE FUNCTION ( $\phi$ ).

32. The law of molecular attraction given in Art. 5 may be used to obtain a formula for the quantity known as the intrinsic pressure of a substance\*. It is the negative pressure, or force of contraction, caused by the attraction of the molecules upon one another. Since the molecules in a substance as a whole are in equilibrium, the instrinsic pressure plus the external pressure is balanced by an equal and opposite pressure due to the motion of translation of the molecules.

Let us consider an infinitely large mass of matter cut into two parts by an imaginary plane. Conceive a rectangular parallelopiped of infinite length and unit cross-section situated in one part and standing with its base on the plane in question. The opposite part of matter exerts a force of attraction upon the parallelopiped at right angles to the plane. This force of attraction is the intrinsic pressure. It is counterbalanced by the pressure due to the motion of translation of the molecules acting at the surface of contact of the parallelopiped and the opposite portion of matter.

In deducing a formula for the quantity in question use will be made of the notation and the results of the investigation of Art. 6. It will be evident from this investigation that the attraction upon a molecule in the parallelopiped at a distance  $nx_a$  from the plane by the opposite portion of matter, is

$$\sum_{v=-\infty}^{v=\infty} \sum_{n=-\infty}^{n=\infty} \sum_{w=0}^{w=\infty} (\phi) \cdot \frac{(\sum_a^c)^2}{z^b} (nx_a + wx_a),$$

where

$$z = x \sqrt{\{(n+w)^2 + u^2 + v^2\}},$$

and  $x_a$  denotes the distance of separation of the molecules.

\* R. D. Kleeman, *Phil. Mag.* xx. 665 (1910).

If  $W$  denote the foregoing expression, the attraction exerted upon all the molecules lying on the  $x$  axis is equal to  $\sum_{n=1}^{n=\infty} W$ . Since  $1/x_a^2$  rows of molecules stand on one square cm. of the plane, the intrinsic pressure  $P_n$  is given by

$$\frac{1}{x_a^2} \sum_{n=1}^{n=\infty} W,$$

or

$$P_n = \frac{1}{x_a^2} \sum_{n=1}^{n=\infty} \sum_{v=-\infty}^{v=\infty} \sum_{u=-\infty}^{u=\infty} \sum_{w=0}^{w=\infty} \phi\left(\frac{v}{x_c}, \frac{z}{x_c}\right) (\Sigma c_a)^2 \left\{ \frac{n+w}{(n+w)^2 + u^2 + v^2} \right\}^3. \quad (62)$$

Since  $\left(\frac{\rho}{m_a}\right)^{1/3} = 1/x_a$ , the equation may be written

$$P_n = M_6^2 \left(\frac{\rho}{m}\right)^{7/3} (\Sigma c_a)^2, \quad . . . . . (63)$$

where  $M_6^2$  is the same for all substances at corresponding states.

It will be noticed that the expression for the external pressure of a substance given by equation (25) is the same in form as that obtained for the intrinsic pressure.

The equation

$$P_n = \mu_2 P_{nc}. \quad . . . . . (64)$$

can be easily established in the same way as equation (24) in Art. 12, where  $P_{nc}$  denotes the intrinsic pressure of a substance at the critical point, and  $\mu_2$  a quantity which is the same for all substances at corresponding states. Comparing equations (25) and (63) when applied to the critical point of a substance we see that

$$P_n = \mu_3 p_c, \quad . . . . . (65)$$

where  $p_c$  is the critical pressure, and  $\mu_3$  a corresponding state quantity.

33. The intrinsic pressure can very simply be connected with the quantity  $U_c$ , defined in Art. 3. The latter quantity may be regarded as the work done against the intrinsic pressure on separating the molecules of a substance an infinite

distance from one another, supposing that the nature of the molecules does not change during the process. Hence under these conditions we have

$$P_n \cdot \partial v = -\partial U_c,$$

or

$$P_n = -\left(\frac{\partial U_c}{\partial v}\right)_T, \quad . \quad . \quad . \quad . \quad . \quad (66)$$

where  $v$  denotes the volume of a gram of substance.

34. A formula can be obtained \* which gives the intrinsic pressure in terms of quantities which can be measured directly. Neglecting  $u - u_a$  in comparison with  $U_c$  according to Art. 4 so that  $\partial U_c = -\partial U$ , we have, from equations (66) and (47),

$$P_n = T \left(\frac{\partial p}{\partial T}\right)_v - p = -\left(\frac{\partial p}{\partial v}\right)_T \left(\frac{\partial v}{\partial T}\right)_p - p = T \frac{\alpha}{\beta} - p, \quad . \quad . \quad (67)$$

where  $\alpha = \frac{1}{v} \left(\frac{\partial v}{\partial T}\right)_p$  denotes the coefficient of expansion of the substance with change of temperature, and  $\beta = -\frac{1}{v} \left(\frac{\partial v}{\partial p}\right)_T$  the coefficient of compression. All the quantities on the right-hand side of the equation admit of direct measurement.

Table XIII. gives the intrinsic pressures for several liquids at various temperatures calculated by means of the foregoing equation. It was found that the value of  $p$  could be neglected in comparison with that of  $T \frac{\alpha}{\beta}$ . The values obtained are principally of interest on account of their great magnitude, being all of the order of 1000 atmospheres. They illustrate the important part played by the molecular forces in determining the state of a substance.

The equation  $P_n = \mu_3 p_c$ , obtained in the previous Article, where  $\mu_3$  is a corresponding state quantity, may now be tested by the facts. It follows from this equation that the ratio of the critical pressures of two substances is equal to the ratio of their intrinsic pressures at corresponding temperatures.

\* R. D. Kleeman, *Proc. Camb. Phil. Soc.* xvi. (6) 540 (1912).

For example, the intrinsic pressures of ether and benzene in the liquid state at temperatures corresponding to  $2T_c/3$  are 2756 and 3892 atmos. respectively, and their ratio is equal to .708. The corresponding ratio of the critical pressures is .733.

TABLE XIII.

$t^\circ \text{C.}$	$\beta 10^6.$	$\alpha.$	$P_n = \frac{T\alpha}{\beta}$ atmos.	$P_n$ equa. (174).
Ether.				
13.5	169	.001574	2669	2502
63	300	.001809	2026	1944
99	539	.001992	1375	1543
Benzene.				
15.4	87	.001215	4083	3616
78.8	126	.001379	3850	2929
Chloroform.				
0	101	.001107	2991	3992
60	204	.001670	2726	3295
Pentane.				
0	229	.001465	1747	2328
60	486	.001830	1260	1761

The two ratios are thus approximately equal to each other, and the foregoing equation is thus satisfied.

35. It may be pointed out at this stage that relations connecting various quantities may be obtained by the help of equations (23), (25), (26), (48), and (63) and the equations  $p=r_1/p_c$ ,  $v=r_2v_c$ , and  $T=r_3T_c$ , given in Art. 10. For example, from the equation

$$\beta = -\frac{1}{v} \frac{\partial v}{\partial p},$$

it may be deduced that

$$\beta = B_1 \left( \frac{m}{\rho} \right)^{7/3} (\Sigma c_a)^{-2} = \frac{B_2}{\rho U_c} = \frac{B_3}{p} = \frac{B_4}{P_n}, \dots \dots (68)$$

where  $B_1$ ,  $B_2$ ,  $B_3$ , and  $B_4$  are quantities which have the same values for all substances at corresponding states. Similarly other relations may be obtained.



36. We have seen in Art. 7 that the law of molecular attraction cannot be completely determined from latent heat data since the process corresponds to finding the equation of a line passing through two points on an isothermal. Data referring to intrinsic pressure, specific heat, etc., however, furnish additional points, and hence by the help of these data information about the form of  $(\phi)$  in the law of attraction may be obtained. It is found that, as a first (rough) approximation, it may be taken as a constant. Assuming this to be the case, the formula for the intrinsic pressure becomes

$$P_n = 1.65 \times 10^5 \left( \frac{\rho}{m} \right)^{7/3} \left( \sum \sqrt{a_w} \right)^2, \quad . . . . (69)$$

where the numerical constant has been determined from the facts. The intrinsic pressures of ether, for example, at  $13.5^\circ \text{C}$ . and  $9.9^\circ \text{C}$ . given by this formula are 2595 and 1760 atmos. respectively, while the experimental values are 2669 and 1375 atmos.

If a formula for the internal heat of evaporation is obtained making the same assumptions it assumes the form

$$L = A_4 \left\{ \left( \frac{\rho_1}{m} \right)^{4/3} - \left( \frac{\rho_2}{m} \right)^{4/3} \right\} \left( \sum \sqrt{a_w} \right)^2, \quad . . . (70)$$

where  $A_4$  is a constant. An application to the facts shows that  $A_4$  is only approximately constant, it decreases with increase of temperature. This suggests that  $(\phi)$ , or the molecular attraction, decreases with increase of temperature, and this has been also shown to follow from specific heat data of gases\*.

37. A formula for the specific heat of liquids, making the same assumption, will now be obtained†. By means of an isothermal cycle it can easily be shown that

$$c_i - c_{ig} = - \frac{\partial u_c}{\partial T}, \quad . . . . (71)$$

where  $c_i$  and  $c_{ig}$  denote the internal specific heats of the

\* R. D. Kleeman, *Proc. Camb. Phil. Soc.* xvi. (6) 540 (1912).

† *Loco. cit.*

condensed and gaseous states respectively. The expression for  $U_e$  is the same as that for  $L$  given by equation (70), and considering the case of a liquid in contact with its vapour at temperatures for which  $\rho_2$  may be neglected in comparison with  $\rho_1$ , we have, from equations (71) and (70),

$$c_i - c_{ig} = -A_4 \frac{4}{3} \frac{\rho_1^{1/3}}{m^{7/3}} \frac{\partial \rho_1}{\partial T} (\Sigma \sqrt{a_w})^2.$$

On eliminating  $A_4$  from this equation by means of equation (70) we finally have

$$c_i - c_{ig} = -\frac{4}{3} \frac{L \rho_1^{1/3}}{\rho_1^{1/3} - \rho^{4/3}} \frac{\partial \rho_1}{\partial T} \dots \dots \dots (72)$$

Table XIV. gives the values of  $c_i$  calculated for a number of liquids by means of the foregoing equation. The experimental values of  $\text{CO}_2$  were taken from a paper by Dieterici \*,

TABLE XIV.

$t^\circ\text{C.}$	$-\frac{d\rho_1}{dT}$	$c_i$ (exp.).	$c_i$ (cal.).	$t^\circ\text{C.}$	$-\frac{d\rho_1}{dT}$	$c_i$ (exp.).	$c_i$ (cal.).
Sulphur dioxide.				Carbon dioxide.			
0	·0025	·317	·316	0	·00409	·495	·466
40	·00285	·342	·325	15	·00901	·691	·731
120	·0055	·457	·462	20	·01064	·806	·814
140	·00887	·568	·579	27	·01800	1·105	1·02
145	·01175	·845	·805	29	·02818	1·48	1·10
153	·0202	1·035	1·207	30	·05047	1·85	2·00
Ether.				Carbon dioxide.			
0	·00114	·529	·632	0	·00146	·2352	·256
80	·00141	·690	·648	30	·00150	·2401	·258
120	·00176	·803	·682	80	·00163	·260	·263
140	·00210	·822	·714	120	·00183	·276	·271
180	·00497	1·041	·961	160	·00201	·2882	·274

and those of the remaining substances from Landolt and Bernstein's Tables, 2nd ed. A fair agreement between calculation and experiment is obtained, and a useful equation for calculating specific heats is thus obtained.

38. Another formula of interest and importance depending

\* *Ann. d. Phys.* xii. 170 (1903).

on the assumption that  $(\phi)$  is constant, which corresponds to the attraction between two molecules varying inversely as the fifth power of their distance of separation, may be obtained in connexion with diffusion of gases \*. Maxwell has shown † that if the attraction between two molecules is given by  $Bz^5$ , where  $B$  is a constant depending on the nature of the attracting molecules and  $z$  is their distance of separation, the coefficient of diffusion  $D$  of a molecule  $r$  in a gas consisting of molecules  $s$  is given by

$$D = \frac{p_r}{\rho_r \rho_s} \frac{p_s}{A_x \left\{ \frac{B}{m_r m_s (m_r + m_s)} \right\}^{1/2}} \frac{1}{p}, \quad \dots \quad (73)$$

where  $p_r$  and  $p_s$  denote the partial pressures and  $\rho_r$  and  $\rho_s$  the partial densities of the gases,  $m_r$  and  $m_s$  denote their molecular weights,  $p = p_r + p_s$ , and  $A_x$  is a constant. Let us consider the case when the number of molecules  $r$  per cubic cm. is small in comparison with the number of molecules  $s$ , so that  $p = p_s$ . Assuming that  $(\phi)$  in the law of molecular attraction may be taken approximately a constant or a function of the temperature only  $B = X \Sigma \sqrt{a_r} \Sigma \sqrt{a_s}$ , where  $X$  is a function of the temperature,  $a_r$  the atomic weight of an atom in a molecule  $r$ , and  $a_s$  that of an atom in a molecule  $s$ . Hence, since

$$\frac{p_r}{\rho_r} = \frac{RT}{m_r}, \quad \text{and} \quad \frac{p_s}{\rho_s} = \frac{RT}{m_s},$$

the equation may be written

$$D = \frac{R^2 T^2}{A \ X^{1/2} p_s} \left\{ \frac{m_r + m_s}{m_r m_s \Sigma \sqrt{a_r} \Sigma \sqrt{a_s}} \right\}^{1/2} \\ = K_s \left\{ \frac{m_r + m_s}{m_r m_s \Sigma \sqrt{a_r} \Sigma \sqrt{a_s}} \right\}^{1/2}, \quad \dots \quad (74)$$

where  $K_s$  is a quantity which is constant at constant temperature and pressure.

\* R. D. Kleeman, *Phil. Mag.* xix, 783 (1910).

† Maxwell's *Collected Papers*, ii. 36; see also J. J. Thomson's *Conduction of Electricity through Gases*, 2nd ed. 372.

The coefficients of inter-diffusion of gases are usually measured at constant pressure and temperature in which  $K_s$  remains constant. Table XV. contains a set of values taken from Meyer's *Kinetic Theory of Gases*, and the values calculated by means of equation (74), giving  $K_s$  a value which renders the calculated coefficient of diffusion equal to that obtained by experiment in the case of  $N_2O$ — $CO_2$ . The agreement between calculation and experiment is, on the whole, fair. The deviations obtained are probably principally due to the inverse fifth power law being only approximately true, and the

TABLE XV.

The gases on left diffuse into gases on right.	Exper. coef. of diffusion.	Calc. coef. diffusion.
$N_2O$ — $CO_2$ .....	·089	·089
Air — $CO_2$ .....	·142	·125
$CH_4$ — $CO_2$ .....	·159	·151
$CO$ — $CO_2$ .....	·160	·125
$O_2$ — $CO_2$ .....	·161	·160
$CO$ — $O_2$ .....	·180	·116
$H_2$ — $SO_2$ .....	·480	·655
$H_2$ — $CO_2$ .....	·556	·723
$H_2$ — $CO$ .....	·642	·904
$H_2$ — $O_2$ .....	·722	·871

diffusion being influenced by the actual volume of the molecules. Remembering this and considering the extremely complicated nature of the process of the diffusion, the agreement between observation and calculation by a formula of such simplicity is perhaps better than can be expected.

39. If we consider the diffusion of a molecule in a gas of the same kind,

$$\Sigma \sqrt{a_r} = \Sigma \sqrt{a_s}, \quad m_r = m_s, \text{ etc.},$$

and equation (74) may be written

$$D = \frac{C_1 T}{m^{1/2} \Sigma \sqrt{a_w}}, \quad \dots \dots \dots (75)$$

using the usual notation, where  $C_1$  is constant for a constant volume of the gas. This coefficient of diffusion cannot be measured in practice. But we can transform the equation into a form which is more useful\*. According to the Kinetic Theory of Gases  $D = \eta/\rho$ , where  $\eta$  denotes the coefficient of viscosity and  $\rho$  the density of the gas. Therefore since  $\rho$  is proportional to  $m$  equation (75) may be written

$$\eta = \frac{C_2 T m_1^2}{\Sigma \sqrt{a_w}}, \quad . . . . . (76)$$

where  $C_2$  is constant at constant volume of the gas.

It is most convenient to apply equation (76) to substances at corresponding states, since  $(\phi)$  has then the same value for each substance if it varies with the temperature. Table XVI. gives the values of  $\eta$  for a few substances corresponding to  $\frac{349}{556} T_c$ , and the values of  $\eta$  calculated by equation (76) writing  $C_2 = 10.25$ . The agreement between calculation and experiment is fair, though not so good as that obtained in the previous Article with equation (74).

TABLE XVI.

Name of substance.	$\eta$ (exp.).	$\eta$ (cal.).
Carbon tetrachloride . . . . .	1950	1630
Chloroform . . . . .	1905	1681
Ethyl propionate . . . . .	1074	1006
Benzene . . . . .	1057	1194
Methyl formate . . . . .	998	1284
Ethyl oxide . . . . .	745	969

40. Since, according to the previous three Articles, as a first approximation  $(\phi)$  may be taken as a constant, and as a second approximation a function of the temperature only, it will be useful to obtain its absolute value for a given temperature. It can be most conveniently calculated by means

\* R. D. Kleeman, *Proc. Camb. Phil. Soc.* xvi. 586 (1912).

of equation (14) applied to a substance at a low temperature, in which case we have approximately  $L=U_{a1}$ . The value of  $U_{a1}$  is given by equation (12) in the form of an infinite convergent series, of which, however, only a few terms need be retained \*. The above equation thus becomes

$$L=1.58 \left( \frac{\rho_1}{m_a} \right)^{4/3} (\Sigma \sqrt{a_w})^2. \quad . \quad . \quad . \quad . \quad . \quad (77)$$

In the case of ether at  $\frac{2}{3}T_c$  we have  $L=75.4 \times 4.6 \times 10^7$  ergs,  $\rho_1=.6907$ ,  $\Sigma \sqrt{a_w}=27.8$ ,  $m_a=74 \times 1.65 \times 10^{-24}$  grm., where  $1.65 \times 10^{-24}$  grm. is the mass of a hydrogen atom obtained by Millikan. We obtain accordingly

$$(\phi)=2.97 \times 10^{-45}$$

for the substance at the temperature  $\frac{2}{3}T_c$ .

It appears from the preceding Articles of this Chapter that  $(\phi)$  in the law of molecular attraction varies little with the temperature and the distance of separation of the attracting molecules. The exact form of  $(\phi)$  may be obtained from the equation of state of a substance by a method which will be explained in Chapter VI. In the remaining part of the chapter some properties of the function  $(\phi)$  will be considered in connexion with the Joule-Thomson effect.

41. The nature of the deviations from Boyle's law obtained with hydrogen in the gaseous state indicates that for certain temperatures and distances of separation of the molecules the intrinsic pressure is negative, or the molecules repel one another. This suggests that the function in the law of molecular attraction consists of a number of positive and negative terms corresponding to forces of attraction and repulsion between the molecules which appear to act independent of one another, the force between two molecules for any particular distance of separation being the resultant of these forces. The force between two molecules would in that case

\* *Loco. cit.* 593.

pass through zero and change in sign for certain distances  $z$  of separation corresponding to  $(\phi)=0$ .

This property of the molecular forces can be experimentally investigated by allowing a mass of  $\phi$  gas to expand from a density  $\rho_3$  to a density  $\rho_4$  over a large range of values of  $\rho_3$  and  $\rho_4$  without allowing it to do external work, and measuring the heating or cooling effect  $L_x$  produced. If the expansion takes place adiabatically and without external work being done, the heating or cooling effect is approximately given by  $L_x/c_v$  where  $c_v$  denotes the average specific heat at constant volume. Experiments of this nature have been carried out, and the change in temperature obtained is known as the Joule-Thomson effect.

The equation giving  $L_x$  may be written

$$L_x = \left\{ \phi_2 \left( \frac{T}{T_c}, \frac{\rho_3}{\rho_c} \right) \rho_3^{4/3} - \phi_2 \left( \frac{T}{T_c}, \frac{\rho_4}{\rho_c} \right) \rho_4^{4/3} \right\} \frac{(\Sigma \sqrt{a_m})}{m^{7/3}}, \quad (78)$$

according to equation (15), where  $\Sigma c_a$  is replaced by  $\Sigma \sqrt{a_w}$  (Art. 18) and  $m_a$  by  $m$ . It follows\* from this equation that the Joule-Thomson effect of substances at corresponding temperatures, when the initial and final densities during expansion are corresponding densities, is proportional to  $\rho c^{4/3} \frac{(\Sigma \sqrt{a_w})^2}{c_v m^{7/3}}$ . A heating effect indicates that over a certain

region of separation the molecules repel one another, the region lying between the initial and final distances of separation during expansion, and a cooling effect indicates that over a certain region they attract one another. Now experiment has shown that both a heating and a cooling effect can be obtained†. It follows, therefore, that the function  $(\phi)$  consists of a number of positive and negative terms.

The points of inversion of a gas—that is, for which there

\* R. D. Kleeman, *Proc. Camb. Phil. Soc.* xvi. (6) 555 (1912).

† P. Joule and Lord Kelvin, *Phil. Mag.* (4) iv. 1852; *Phil. Trans.* 1853, 1854, 1862; Joule's *Scientific Papers*, ii.

is no heating or cooling effect for a small expansion—are given by the equation

$$\frac{\partial U_c}{\partial \rho} = 0 \quad \text{or} \quad \frac{\partial}{\partial \rho} \left\{ \phi_2 \left( \frac{T}{T_c}, \frac{\rho}{\rho_c} \right) \rho^{4/3} \right\} = 0, \quad . \quad . \quad . \quad (79)$$

obtained from equation (12).

According to this equation the point of inversion depends on the density as well as the temperature of the substance. Further, if a number of substances have corresponding densities their points of inversion will occur at corresponding temperatures. This condition has probably been approximately fulfilled in experiments on the subject since gases with a low critical temperature were found to have a low temperature of inversion. Thus a remarkable explanation of the Joule-Thomson effect in the connexion with the law of molecular attraction stated in Art. 5 is furnished.

42. It has been found that the cooling effect obtained with gases can be approximately represented by the equation

$$\frac{dT}{dp} = \frac{\alpha_1}{T^2}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (80)$$

where  $\frac{dT}{dp}$  is the change in the temperature of the gas per unit change in pressure during the expansion, and  $\alpha_1$  is a constant which depends on the nature of the gas. But obviously this equation can only have a very limited range of application. It will be convenient to give the equation a different form. Since a gas may be taken to obey approximately the ideal gas law  $pv = \frac{RT}{m}$ , we have from this equation,  $v \cdot dp + p \cdot dv = \frac{RdT}{m}$ . Now  $dT$  is usually numerically very small in comparison with  $dp$  and  $dv$  in such experiments, and the equation may therefore be written

$$dp = -\frac{p}{v} \cdot dv = -\frac{RT}{mv^2} \cdot dv.$$

The equation giving the cooling effect may therefore be written

$$dT = \frac{R\alpha}{mv^2 T} \cdot dv. \quad . \quad . \quad . \quad . \quad . \quad . \quad (81)$$



Now we may suppose that the expansion at different temperatures of a gas is carried out in such a way that  $dv$  and  $v$  are the same in each case. It follows, then, from the foregoing equation, that the cooling effect of a gas under these conditions varies inversely as its absolute temperature. Now a cooling effect indicates that on expansion some of the molecular kinetic energy is expended in overcoming the attraction between the molecules, and, since the initial and final volumes of the gas are kept constant, a variation of the cooling effect with the temperature indicates that the *molecular attraction varies with the temperature*. Thus equation (81) indicates that the molecular attraction decreases with increase of temperature. This falls into line with the results of Art. 36.

We may suppose that the experiments on the Joule-Thomson effect of different gases expressed by equation (80) were carried out in such a way that the temperature and the initial and final volumes of a gas were the same fractions of the critical temperature and density in each case. Equation (81) may then be written

$$dT = \frac{k_1 \alpha_1 \rho_c}{m T_c}$$

on expressing the quantities  $\rho$  and  $T$  on the right-hand side of the equation in terms of their critical values, where  $k_1$  is the same for all substances, since the experiments are supposed to be carried out at corresponding states. Now we have seen in Art. 41 that if the experiments are carried out under the conditions stated above, the cooling effect is given by an expression which may be equated with the foregoing expression, giving

$$\alpha_1 = -\frac{k_3 \rho_c^{1/3} T_c}{c_v m^{4/3}} (\sqrt{a_w})^2, \quad . . . . . (82)$$

where  $k_3 = k_2/k_1$ , and  $k_3$  is approximately an absolute constant since  $\alpha_1$  was found to be approximately independent of the temperature and density of the gas.

The value of  $\alpha_1$  obtained by experiment may now be compared with that given by theory. Joule has shown that at a temperature of  $17^\circ$   $\alpha_1$  has the value  $\cdot 265$  for air and  $1\cdot 05$  for carbon dioxide. To calculate  $\alpha_1$  we have for carbon dioxide  $\rho_c = \cdot 464$ ,  $T_c = 304$ , and  $c_c = \cdot 1486$  at  $17^\circ$ , and for nitrogen (the principal constituent of air)  $\rho_c = \cdot 37$ ,  $T_c = 127$ , and  $c_c = \cdot 1735$ . On writing  $k_3$  equal to  $7\cdot 544 \times 10^{-4}$  in equation (82) it gives  $\alpha_1 = 1\cdot 03$  for carbon dioxide, and  $\alpha_1 = \cdot 262$  for air. The agreement between calculation and experiment is thus very good. There is evidently an extensive and important field for further experimental research on the Joule-Thomson effect in connexion with molecular forces.

The molecular forces will next be considered in connexion with surface tension.

## CHAPTER IV.

THE SURFACE TENSION, SURFACE ENERGY, TRANSITION REGION,  
AND OTHER PROPERTIES OF LIQUID SURFACES.

43. The surface tension of a liquid is a familiar and striking example of the effect of molecular forces. It lends itself to mathematical treatment from a number of aspects. These investigations furnish some general information on the subject of molecular forces, and some relations between surface tension and other quantities.

The surface tension of a substance may be defined as the external work done in producing unit increase in the area of its surface. This increase in area may be produced in a variety of ways, since it follows from Thermodynamics that the work done during an isothermal process between given limits is independent of the nature of the path of the process. The most useful way for mathematical investigation is the one proposed by Laplace, according to which a mass of matter is supposed to be cut into two parts by an imaginary plane, and these parts then separated by an infinite distance from one another. It will readily be seen that if the surface of a liquid possessed no transition layer, that is, no layer of substance of definite thickness in which the density and other properties change from those of the liquid on one side to those of its vapour on the other, the surface tension could be calculated by Laplace's method of increasing the surface, if the law of molecular attraction were known. A transition layer, however, actually exists, as will be shown in Art. 49. It will be of interest and importance, however, to obtain, by means of the law of molecular attraction given in Art. 5, a formula for the surface tension that would exist if no transition layer were formed.

44. Let us suppose that the imaginary plane cutting the substance into two parts in Laplace's method coincides with one of the planes defining the relative distribution of the molecules in space \*. Let one of the molecules in the plane be taken as zero of coordinates and the same notation adopted as in Art. 6. The attraction of one of these portions of matter on a molecule in the other portion on the  $x$ -axis at a distance  $nx_a$  from the origin is therefore

$$\sum_{v=-\infty}^{v=\infty} \sum_{u=-\infty}^{u=\infty} \sum_{w=0}^{w=\infty} (\phi) \cdot (\Sigma c_a)^2 \frac{ux_a + wx_a}{z^6}.$$

The work done in moving this molecule to infinity is  $\int_n^{\infty} \gamma x_a \cdot dn$ , where  $\gamma$  denotes the foregoing expression. The work done in moving all the molecules on the  $x$ -axis in the same portion of matter to infinity is therefore

$$\sum_{n=1}^{n=\infty} \int_n^{\infty} \gamma x_a \cdot dn.$$

Now  $1/x_a^2$  rows of molecules stand on each cm. of surface of separation of the portions of matter, and the work done in moving them to infinity is therefore equal to twice the surface tension  $\lambda_a$ , or

$$\lambda_a = \frac{1}{2x_a^6} \sum_{n=1}^{n=\infty} \int_n^{\infty} \sum_{v=-\infty}^{v=\infty} \sum_{u=-\infty}^{u=\infty} \sum_{w=0}^{w=\infty} (\phi) \cdot (\Sigma c_a)^2 \frac{n+w}{k_a^6} \cdot dn, \quad (83)$$

where

$$z = x_a \sqrt{\{(n+w)^2 + u^2 + v^2\}} = x_a k_a,$$

and  $x_a$  is the distance of separation of the molecules. Since  $1/x_a = (\rho/m_a)^{1/3}$ , where  $\rho$  denotes the density of the substance, and  $1/x_c = (\rho_c/m_a)^{1/3}$ , the equation may be written

$$\lambda_a = \kappa_1^2 \left(\frac{\rho}{m}\right)^2 (\Sigma c_a)^2, \quad . . . . . (84)$$

where  $\kappa_1$  is the same for all substances at corresponding states.

The foregoing expression for surface tension applies strictly

\* R. D. Kleeman, *Phil. Mag.* xviii. 491, 901 (1909); xix. 783 (1910).

only to a substance not surrounded by its own vapour, or other matter, besides possessing no surface transition layer. If the substance is a liquid of density  $\rho_1$ , surrounded by its own vapour of density  $\rho_2$ , we may suppose that in separating the portions of matter an amount of matter of density  $\rho_2$  remains stationary in space. The surface tension in such a case is thus the same as that of a substance of density  $\rho_1 - \rho_2$  not surrounded by any vapour. A more general formula for the surface tension than the one given above is therefore

$$\lambda_a = \kappa_1^2 \left( \frac{\rho_1 - \rho_2}{m} \right)^2 (\Sigma c_a)^2 \quad . \quad . \quad . \quad . \quad . \quad (85)$$

But it will be observed that this equation holds strictly only if the molecules of matter are infinitely small in size, for otherwise the distribution of the molecules in space that are removed is not the same as that of the molecules of the equivalent substance of the same density, a condition that has to be satisfied if the above equation is to hold strictly. The deviations of the formula through this condition not being satisfied will obviously be the greater, the smaller the difference between the density of the substance and that of its vapour, and thus greatest near its critical point.

Since  $\rho_2 = \rho_1 e_2/e_1$ , Art. 10, where  $e_2/e_1$  is the same for all substances at corresponding states, the above equation may be written

$$\lambda_a = \kappa_2^2 \left( \frac{\rho_1}{m} \right)^2 (\Sigma c_a)^2, \quad . \quad . \quad . \quad . \quad . \quad (86)$$

where  $\kappa_2$  is the same at corresponding states. This is the fundamental surface tension equation corresponding to no transition layer.

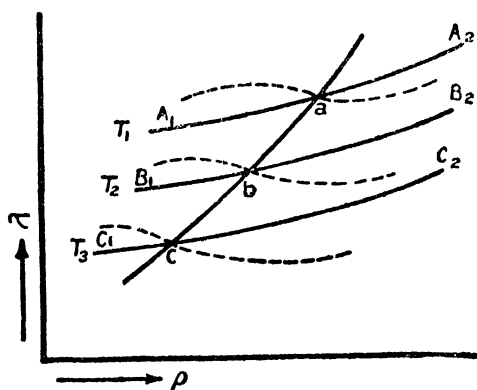
The relation

$$\lambda_a = \mu_4 \lambda_o, \quad . \quad . \quad . \quad . \quad . \quad (87)$$

where  $\lambda_o$  denotes the surface tension at the absolute zero of temperature, and  $\mu_4$  a corresponding state quantity, can be easily established in the same way as equation (24) in Art. 12.

45. It will be of importance next to discuss the foregoing equations in connexion with determining the law of molecular attraction from surface-tension data, supposing that the equations represent the facts. We have seen in Art. 7 that the law of molecular attraction cannot be completely determined from latent-heat data. It will now be shown that for surface-tension data this also holds \*. To simplify matters, let us suppose that the data refer to low temperatures, at which the presence of the vapour does not affect the surface tension, and the effect of the surface transition layer may be neglected (Arts. 52 and 53), in which case the foregoing equations would apply. Now, according to Art. 7, the molecular attraction must initially be taken a function of *two independent variables*,

Fig. 5.



the temperature and distance of separation of the molecules, and the surface tension  $\lambda_a$  is therefore given by an equation of the form

$$\lambda_a = \psi(\rho, T),$$

where  $T$  denotes the temperature and  $\rho$  the density of the substance. In this equation  $T$  and  $\rho$ , it should be noted, are *independent variables*.

Let the curves  $A_1, A_2, B_1, B_2 \dots$  in fig. 5 represent the graphs connecting  $\lambda_a$  and  $\rho$  of a substance according to the

\* R. D. Kleoman, *Phil. Mag.* xxi. 83 (1911).

foregoing equation, corresponding to the temperatures  $T_1, T_2, \dots$  which stand in ascending order of magnitude. Let the abscissæ of the points  $a, b, c, \dots$  denote the values of  $\rho$  of the substance in liquid form in contact with its saturated vapour corresponding to these temperatures. The ordinates of these points then give the corresponding surface tensions of the liquids. Now it is obvious that any equation connecting  $T, \rho$ , and  $\lambda_a$  which gives rise to a set of curves corresponding to different values of  $T$  passing through the points  $a, b, c, \dots$  without necessarily coinciding with any other parts of the curves  $A_1, A_2, B_1, B_2, \dots$  expresses a formula for the surface tension. It is obvious from the figure that an infinite number of such sets of curves, indicated by dotted lines, and the corresponding surface tension equations, can be obtained. It follows therefore in the same way as in Art. 7 that the law of molecular attraction cannot be completely determined from surface-tension data, or the law deduced from such data must contain an arbitrary function.

If an equation connecting  $\lambda_a$  and  $\rho$  for a liquid can be found representing the facts, this does not indicate that  $\lambda_a$  is independent of  $T$ . For each of the equations representing a set of curves in fig. 5 could be transformed into an equation connecting  $\lambda_a$  and  $\rho$  only, by means of the relation that must exist between  $\rho$  and  $T$ . This does not, however, signify that the quantities of  $\rho$  and  $T$  are dependent in the fundamental surface-tension equation.

Thus we see that no definite information about the law of molecular attraction can be obtained from surface-tension data alone, even if a transition layer did not exist on a liquid surface. The same result would obviously also hold if, as is the case in practice (Art. 49), a transition layer exists.

46. It follows from the results of the preceding Article that an infinite number of different expressions for the surface tension in terms of the temperature  $T$  and the densities  $\rho_1$  and

$\rho_2$  of the liquid and vapour may be obtained agreeing with the facts. If these various expressions are equated an infinite number of equations connecting  $\rho_1$ ,  $\rho_2$ , and  $T$  are obtained. But two only are independent (Art. 8). They express the relations existing between the foregoing quantities. Thus three of the surface-tension equations are in form independent of each other. The two equations obtained from them, giving the relations between  $\rho_1$ ,  $\rho_2$ , and  $T$ , should be the same as those obtained along the same lines from three independent equations giving the internal heat of evaporation (Art. 8).

This result may be put into a mathematical form. The three independent latent-heat equations may be written in the general forms

$$\left. \begin{aligned} L_1 &= \phi_1(\rho_1, \rho_2, T) \cdot \psi_1(\rho_1, \rho_2, T) \\ L &= \phi_1(\rho_1, \rho_2, T) \cdot \psi_2(\rho_1, \rho_2, T) \\ L &= \phi_1(\rho_1, \rho_2, T) \cdot \psi_3(\rho_1, \rho_2, T) \end{aligned} \right\} \dots \dots \dots (88)$$

From these the two equations

$$\left. \begin{aligned} \psi_1(\rho_1, \rho_2, T) &= \psi_2(\rho_1, \rho_2, T) \\ &= \psi_3(\rho_1, \rho_2, T) \end{aligned} \right\} \dots \dots \dots (89)$$

connecting  $\rho_1$ ,  $\rho_2$ , and  $T$  may be obtained. The three independent surface-tension equations accordingly are

$$\left. \begin{aligned} \lambda &= \phi_2(\rho_1, \rho_2, T) \cdot \psi_1(\rho_1, \rho_2, T) \\ \lambda &= \phi_2(\rho_1, \rho_2, T) \cdot \psi_2(\rho_1, \rho_2, T) \\ \lambda &= \phi_2(\rho_1, \rho_2, T) \cdot \psi_3(\rho_1, \rho_2, T) \end{aligned} \right\}, \dots \dots \dots (90)$$

since they also yield equations (89). Thus the surface-tension equations may be obtained from the latent-heat equations on replacing the factor  $\phi_1(\rho_1, \rho_2, T)$  by  $\phi_2(\rho_1, \rho_2, T)$  and  $L$  by  $\lambda$ .

47. The equations obtained in Art. 44 apply only, we have seen, to an ideal liquid surface possessing no transition layer. It will be shown in Art. 49 that in practice a transition layer exists, and a formula is obtained for the work required for its formation. It will be of interest and importance notwithstanding, to test whether equations similar in form to the fore-



going apply to the surface tension modified by the transition layer. Thus let us apply the equation

$$\lambda = \kappa_s^2 \left( \frac{\rho_1}{m} \right)^2 (\Sigma c_a)^2 \dots \dots \dots (91)$$

to the facts, which is similar to equation (86), where  $\lambda$  denotes the surface tension found in practice, and  $\kappa_s$  a quantity which is the same for all substances at corresponding states. The quantities  $\kappa_s$  and  $\kappa_2$  are not, of course, identical. Table XVII. contains \* the experimental values of  $\lambda^{1/2} \frac{m}{\rho_1}$  for a few liquids at

TABLE XVII.

Name of liquid.	$\frac{\lambda^{1/2} m}{\rho_1}$ .	$\kappa_s \Sigma c_a$ .
Ether .....	404.2	398.7
Methyl formate .....	287.7	285.3
Carbon tetrachloride ....	437.5	417.6
Benzene .....	421.6	405.8
Chlorobenzene .....	493.7	485.2
Ethyl acetate .....	435.1	440.4
Propyl acetate .....	502.5	519.3

temperatures corresponding to  $\frac{2}{3}T_s$ , and the values of this expression given by the above equation, giving to  $\kappa_s$  the value 10.74, and using the values of  $c_a$  given in Table II. Art. 11. The results show that this equation represents the facts very well.

The equation similar to equation (87) in Art. 44 corresponding to the results of the previous Article is

$$\lambda = \mu_s \lambda_0, \dots \dots \dots (92)$$

where  $\lambda_0$  denotes the surface tension at the absolute zero of temperature and  $\mu_s$  a corresponding state quantity. According to this equation the ratio of the surface tensions of a liquid for two different temperatures should be the same as a similar ratio for another liquid at corresponding temperatures. This

\* R. D. Kleeman, *Phil. Mag.* xviii. 501 (1909). The values of  $\lambda$  were taken from a paper by Ramsay and Shield, *Phil. Trans. of Roy. Society*, xxxiv. 647 (1893).

is tested \* in Table XVIII., which contains the values of the ratios  $\lambda_1/\lambda_2$ ,  $\lambda_1/\lambda_3$ ,  $\lambda_1/\lambda_4$ , and  $\lambda_1/\lambda_5$  for a number of liquids, where the suffixes 1, 2, 3, 4, and 5 refer to the five sets of tempera-

TABLE XVIII.

Name of liquid.	$\lambda_1/\lambda_2$ .	$\lambda_1/\lambda_3$ .	$\lambda_1/\lambda_4$ .	$\lambda_1/\lambda_5$ .
Ether .....	1.153	1.430	2.146	3.996
Methyl formate.....	1.152	1.421	2.111	3.913
Carbon tetrachloride....	1.173	1.412	2.086	3.828
Benzene .....	1.150	1.422	2.119	3.818
Chlorobenzene .....	1.174	1.416	2.112	3.891

tures corresponding to  $\frac{2}{3}T_c$ ,  $\frac{1}{2}T_c$ ,  $\frac{3}{4}T_c$ ,  $\frac{5}{7}T_c$ , and  $\frac{8}{9}T_c$  respectively. It will be seen that the ratios are fairly constant for each set of corresponding temperatures.

48. The effect of the transition layer on the magnitude of the surface tension of a liquid can be mathematically investigated. Suppose that, on separating the two portions of a liquid in the process described in Art. 43, no change takes place in the distribution of the molecules in the surfaces of the slabs. Let the work done per unit area, which is the corresponding surface tension, be denoted as before by  $\lambda_a$ . Now suppose that the surface transition layers are formed. This requires that the surface layer of the liquid undergoes expansion in different degrees in the various layers into which it can be divided. Since the complete process of increase of the surface of a liquid is a reversible one, we must suppose that the formation of the transition layer in the foregoing process takes place in such a way that external work is done. To realize this we may suppose that the liquid is contained in a cylinder having a piston in contact with the liquid surface under consideration exerting a pressure tending to prevent the formation of the layer. Accordingly work is done on the piston during the formation of the layer, which is done at the expense of the heat supplied, since the temperature is kept constant during the process.

\* R. D. Kleeman, *Phil. Mag.* xviii. 498 (1909).



The difference  $\lambda_a - \lambda$  represents the work performed in the formation of the transition layer per square cm. of surface. It will be seen that its magnitude is somewhat less than that of  $\lambda$ , and is approximately independent of the temperature over the regions of temperature considered.

TABLE XIX.

Ethyl oxide, $C_2H_5O$ .					
T.	L.	$\rho_1$ .	$\lambda_a$ .	$\lambda$ .	$\lambda_a - \lambda$ .
313	75.36	.6894	23.12	14.05	9.07
333	70.79	.6658	21.20	11.80	9.40
353	65.85	.6402	19.27	9.67	9.60
373	60.33	.6105	17.16	7.63	9.53
Carbon tetrachloride, $CCl_4$ .					
363	40.62	1.4554	26.18	17.60	8.58
383	38.64	1.4124	24.41	15.41	9.00
403	36.58	1.3680	22.62	13.27	9.35
423	34.42	1.3215	20.81	11.21	9.60
Methyl formate, $C_2H_4O_2$ .					
303	107.5	.9598	38.35	23.09	15.26
333	95.59	.9133	32.98	18.58	14.40
363	85.10	.8636	28.25	14.29	13.96
Benzene, $C_6H_6$ .					
353	85.62	.8415	29.87	20.28	9.59
383	80.05	.7809	27.15	16.86	10.29
413	74.09	.7440	24.33	13.45	10.88

Equation (94) applies strictly only when the substance under consideration is not surrounded by matter, and applies very approximately when the density of the surrounding matter is comparatively small. In the case that the substance is surrounded by matter of the same kind, for example, a liquid of density  $\rho_1$  surrounded by its vapour of density  $\rho_2$ , it may be supposed that we are dealing with a substance of density  $\rho_1 - \rho_2$  not surrounded by matter (Art. 44). The value of  $U_c$  is, as before, equal to  $L$ , the internal heat of evaporation. Equation (94) then becomes

$$\lambda_a = \frac{Lm_a^{1/3}}{6 \times 876} (\rho_1 - \rho_2)^{2/3} \quad . \quad . \quad . \quad . \quad . \quad (95)$$

The values of  $\lambda_a$  given by this equation in the case of ether for higher temperatures than those considered in Table XIX. are contained in Table XX. It will be seen that they decrease

TABLE XX.

Ethyl oxide,  $C_4H_{10}O$ .

T.	L.	$\rho_1$ .	$\rho_2$ .	$\lambda_a$ .	$\lambda$ .	$\lambda_a - \lambda$ .
383	58.07	.5942	.02349	15.70	6.63	9.07
413	48.31	.5385	.04488	11.86	3.77	8.09
443	34.18	.4658	.08731	7.03	1.33	5.70
463	18.11	.3663	.1620	2.47	.16	2.31
466	12.03	.3300	.2012	1.21	.04	1.17

as the critical point is approached, as we might expect, since  $\lambda_a$  at the critical point should be equal to zero. The values of the work performed in the formation of a transition layer also decrease, which we would expect for a similar reason. But it will be seen that the ratio  $\lambda_a - \lambda / \lambda_a$ , or the proportion of energy obtained in the formation of a transition layer, rapidly increases with increase of temperature, especially near the critical point. This result will be found to fall into line with the considerations in Art. 48.

50. The investigation in the previous Article shows that there is a considerable difference between the surface tension found in practice and that which would exist if no transition layer were formed. This difference represents the energy absorbed in the formation of the layer, and was denoted by  $w$ . Since the expressions for  $\lambda_a$  and  $\lambda$  have the same general form (Arts. 46 and 57) and  $w = \lambda_a - \lambda$ , it follows that  $w$  also has the same general form, that is, we may write

$$w = \kappa_4 \left( \frac{\rho}{m} \right)^2 (\Sigma c_a)^2, \quad . \quad . \quad . \quad . \quad . \quad . \quad (96)$$

where  $\kappa_4 = \kappa_2 - \kappa_3$ , and  $\kappa_4$  is a quantity which has the same value for all substances at corresponding states. Thus  $\lambda_a$ ,  $\lambda$ , and  $w$  may be said to possess similar properties.

51. The quantity  $w$ , it should be pointed out, does not only represent the energy spent in producing a change in the density of the surface layer of a substance, but also the energy spent in other ways. It includes the energy necessary to produce a double layer of electricity which appears to exist on the surface of a substance. This layer manifests itself by the electrical effects obtained on bubbling gases through liquids, the volta effect, and the displacement of the interface of two liquids by an electric current, which forms the basis of the capillary electrometer. If the molecules are not symmetrical in form, which is highly probable, the average relative grouping of the molecules may be different at the surface of a substance from that which obtains in the interior. This change in grouping of some of the molecules on change of surface area would take place at the expense of the energy represented by  $w$ . Besides, the molecules near the surface may be in a different condition than the molecules in the interior of the liquid on account of being less under the influence of the attraction of the surrounding molecules. The thickness of the transition layer is thus the depth over which the substance differs (in various ways) from the substance in the interior.

An approximate value of the thickness of the transition layer of a liquid may be obtained. Consider the molecules lying in an imaginary plane cutting a liquid into two parts. They exert a pressure due to their motion of translation which is balanced by the attraction of the two portions of liquid upon one another, called the intrinsic pressure. Now consider the single layer of molecules lying on the surface of a liquid which has no transition layer. The molecules exert a pressure equal to the intrinsic pressure, and a pressure equal to this amount would have to be applied to prevent the formation of the layer. The average pressure exerted during the formation of the layer may therefore, as a first approximation, be taken equal to—say one-third of the intrinsic pressure. The

thickness  $x$  of the layer is thus approximately given by

$$x \frac{P_n}{3} = w, \quad . . . . . (97)$$

where  $P_n$  denotes the intrinsic pressure and  $w$  the external work done in the formation of the layer. For example, in the case of ether at  $13^\circ \text{C}$ . we have  $P_n = 2.669 \times 10^9$  dynes,  $w = 9.07$  ergs, and hence  $x = 10^{-8}$  cm. The thickness of the transition layer of a liquid is thus very small, being of the same order of magnitude as the diameter of a molecule, or the distance of separation of the molecules of a liquid. Therefore, if the density were plotted against a line at right angles to the surface of a liquid, it would, at any instant, show a jagged and discontinuous curve, due to the fact that matter consists of molecules and that these are in motion. But if the average density were taken over an infinitely long time, a continuous curve would be obtained indicating a continuous change from the liquid to the gaseous state.

The thickness of the transition layer has been considered only in connexion with changes in density of the substance, since we would expect from the nature of things that the energy spent in producing other changes would be relatively small. It is hardly likely that the latter changes would persist to a much greater depth than that corresponding to the change in density.

52. It can be shown theoretically that no transition layer exists on the surface of a substance at the absolute zero of temperature. We know that the pressure exerted by the molecules due to their motion of translation is zero at that temperature. Therefore when the substance is in a condensed state the attraction between the molecules is balanced by their repulsion upon each other. But the substance may exist besides in the gaseous state, in which case the density has to be infinitely small, so that the forces the molecules exert upon

each other may be infinitely small. A substance of intermediate density cannot therefore under any circumstances exist since there is nothing to counteract the intrinsic pressure. Therefore a transition layer on the surface of a substance, which involves a change in density in passing from one side to the other, cannot exist at the absolute zero of temperature.

53. If no transition layer existed on a liquid surface, equation (95) in Art. 49 could be used to calculate the absolute molecular weight of a molecule \*. But though a transition layer exists, as we have seen, the equation is still of service in obtaining a value of this quantity. Thus it was found that if values of  $m_a$  are calculated by the equation for different temperatures of a liquid on substituting for  $\lambda_a$  in the equation the values of  $\lambda$  found in practice, and these values of  $m_a$  plotted against the corresponding temperatures, the points obtained lie approximately on a straight line. Now we have just seen that the effect of the transition layer on the surface tension decreases with decrease of temperature, and is zero at the absolute zero of temperature. The value of  $m_a$  of a substance obtained by means of equation (95) at the absolute zero of temperature would therefore be the true value. This value may be obtained from the line plotted as described, by finding the intercept of its prolongation on the  $m_a$  axis.

The values  $1.67 \times 10^{-24}$ ,  $1.62 \times 10^{-24}$ , and  $1.62 \times 10^{-24}$  in grams for the mass of the hydrogen atom were obtained from carbon tetrachloride, methyl formate, and benzene respectively in this manner. The mean value is

$$1.64 \times 10^{-24} \text{ gram,}$$

which is very nearly equal to  $1.65 \times 10^{-24}$  gram, the value deduced by Millikan from experiments on the charge on the electron.

\* R. D. Kleeman, *Proc. Cam. Phil. Soc.* xvii. (1) 149 (1913).



This result is a striking confirmation of the validity of equation (95) and of the results of Arts. 49 and 51 dealing with the transition layer. It also shows that  $u-u_a$  may be neglected in comparison with  $U_c$  (Art. 4), since in using equation (94)  $U_c$  was taken equal to  $L$ .

54. The surface tension of a mixture of substances that would exist if no transition layer were formed can be found along similar lines to that of a pure substance\*. It is obvious that we may replace the molecules in a mixture by a set of molecules which are the same in every respect, provided the surface tension remains unaltered. Equation (94) in Art. 49 may then at once be applied. Since  $m_a$  in the equation occurs in connexion with the number of molecules in the substance, the average molecular weight must be substituted for  $m_a$ . The quantity  $U_c$  refers to a gram of the substance in all cases, being the energy necessary to separate the molecules of a gram of substance an infinite distance from one another.

If the vapour pressure of the mixture is very small, this holds usually also for the constituents in the pure state. In that case the value of  $U_c$  can be expressed in terms of quantities which can be easily measured. It is then equal to the energy necessary to separate the mixture into its constituents in the liquid form, which is numerically equal to the heat of mixing, and the energy necessary to evaporate the resultant pure liquids. Therefore if the mixture consists of the substances  $a$  and  $b$  in the proportions of  $w_a$  to  $w_b$  by weight we have

$$U_c = \frac{w_a L_a + w_b L_b}{w_a + w_b} - H_{ab}, \quad . \quad . \quad . \quad . \quad . \quad (98)$$

where  $L_a$  and  $L_b$  denote the internal heats of evaporation per gram of the pure substances  $a$  and  $b$  respectively, and  $H_{ab}$  denotes the heat mixture of the constituents of a gram of the mixture.  $H_{ab}$  is usually small in comparison with  $L_a$  and  $L_b$  and may accordingly be neglected.

\* R. D. Kleeman, *Proc. Camb. Phil. Soc.* xvii. (5) 409 (1914).

Table XXI. contains the surface tensions  $\lambda_a$  at different temperatures for two mixtures of liquids corresponding to no transition layer being formed, calculated by means of equations (98) and (94). The Table also gives the surface tensions  $\lambda$  obtained experimentally by Ramsay and Aston. The values of  $\lambda_a - \lambda$ , or the differences between these surface tensions, are equal to the energies expended in the formation of the transition layers.

TABLE XXI.

Mixt. of 1 mol. $C_6H_6$ to 1 mol. $CCl_4$ . Average $m_a = 116 \times 1.61 \times 10^{-21}$ gram.							
T.	$\rho$ .	$\lambda$ .	$L.(C_6H_6)$ .	$L.(CCl_4)$ .	$U_c$ .	$\lambda_a$ .	$\lambda_a - \lambda$ .
289	1.2597	27.70	97.11	46.97	63.84	34.0	6.31
318.2	1.2095	23.50	91.8	44.39	60.27	31.3	7.75
351.2	1.1596	19.71	85.3	41.64	56.27	28.4	8.73
1 mol. $CHCl_3$ to 1 mol. $CS_2$ . Average $m_a = 97.7 \times 1.61 \times 10^{-24}$ gram.							
282	1.4026	29.16	61.41	81.78	69.36	37.48	8.32
317.9	1.3406	24.49	57.30	76.79	64.88	34.02	9.53
334	1.3128	22.23	53.59	74.29	62.82	32.48	10.25

It was found that the value for  $\lambda_a$  for a mixture  $C_6H_6$  and  $CCl_4$  is practically independent of the relative concentrations of the ingredients, if the temperature is kept constant. We have seen in Art. 49 that in the case of pure substances  $\lambda_a - \lambda$  is practically independent of the temperature over a wide range of temperatures. But for mixtures this does not hold, the value of this expression increasing with increase of temperature.

55. A change in the area of the surface of a liquid produces a change in the total internal energy associated with it. If the area is changed by  $\partial A$ , the change  $\partial U$  in internal energy, or the change  $E$  per unit change of surface, is given by the equation

$$\left(\frac{\partial U}{\partial A}\right) = E = -T \left(\frac{\partial \lambda}{\partial T}\right)_A + \lambda, \quad . \quad . \quad . \quad . \quad (99)$$

which is obtained by applying the thermodynamical equation 47) given in Art. 28 to this case, where  $p = -\lambda$  and  $\partial v = \partial A$ .

This equation was first obtained by Lord Kelvin by means of a cyclic process.

A part of the internal energy  $E$  of a liquid surface, which is always a positive quantity, consists, according to equation (99), of the surface tension  $\lambda$ , which represents the increase in the potential energy of attraction brought about by the separation of the molecules on increasing the surface. The part  $-T\left(\frac{\partial \lambda}{\partial T}\right)_A$  therefore represents energy absorbed in the form of heat. This part is also found to be always positive.

56. It can be shown by means of the foregoing equation that a transition layer exists on every liquid surface. For suppose that no transition layer of *any kind* exists. The internal energy  $\left(\frac{\partial U}{\partial A}\right)_T$ , or  $E$ , is then equal to  $\lambda$ , as is evident, if we suppose that the surface is produced by Laplace's method. Under these conditions  $\left(\frac{\partial \lambda}{\partial T}\right)_A = 0$  according to equation (99). But experiment shows that this does not hold, and a liquid surface has therefore a transition layer.

Its existence is therefore associated with a finite value of  $\left(\frac{\partial \lambda}{\partial T}\right)_A$ . Now if a substance possessing no transition layer expands with increase of temperature this term is not zero. Hence it has a transition layer. We may therefore say that the existence of a transition layer is associated with the expansion of a substance with an increase of temperature. The work of formation of a transition layer would thus decrease with decrease of coefficient of expansion, and the thickness of the layer thus decrease with decrease of temperature. It is interesting to compare this result with the conclusions of Art. 52.

57. Equation (99) can be given a form which is of interest \*. On substituting for  $\lambda$  in the equation from equation (91), and

\* R. D. Kleeman, *Phil. Mag.* xviii. 491 (1909).

expressing  $T$  and  $\rho_1$  in terms of the corresponding state quantities  $e_3$  and  $e_1$  by means of the equations  $T=e_3T_c$  and  $\rho_1=e_1\rho_c$  given in Art. 10 we obtain

$$E=\kappa_5^2\left(\frac{\rho_1}{m}\right)^2(\Sigma c_a)^2, \quad . \quad . \quad . \quad . \quad . \quad (100)$$

where  $\kappa_5$  has the same value for all liquids at corresponding states. It will be noticed that this equation has the same general form as equation (91).

Whittaker has calculated \* the values of  $E$  for a number of substances by means of equation (99). The writer has shown that they may be represented by equation (100).

It was also found by trial that  $\kappa_5$  is approximately proportional to the absolute temperature, and since it must be a corresponding state quantity it must be written  $c\frac{T}{T_c}$ , where  $T_c$  is the critical temperature and  $c$  a constant.

58. It follows from equations (100) and (91) that

$$\frac{E}{\lambda_1}=\left(\frac{\kappa_5}{\kappa_3}\right)^2$$

where  $\kappa_5/\kappa_3$  is the same for all liquids at corresponding states. This is found to agree well with the facts.

From equation (100) it can be deduced that

$$E=\mu_6E_0, \quad . \quad . \quad . \quad . \quad . \quad (101)$$

where  $E_0$  refers to the absolute zero and  $\mu_6$  has the same value for all liquids at corresponding states.

59. Various equations may be obtained by the help of equations (23), (25), (26), (48), (63), (91), and (100), and the equations  $p=r_1p_c$ ,  $v=r_2v_c$ , and  $T=r_3T_c$  given in Art. 10. It may be shown, for example, that

$$\lambda_1\beta=D_1\left(\frac{m}{\rho_1}\right)^{1/3} \quad . \quad . \quad . \quad . \quad . \quad (102)$$

$$\lambda\alpha=D_2\left(\frac{\rho_1}{m}\right)^{2/3} \quad . \quad . \quad . \quad . \quad . \quad (103)$$

\* E. T. Whittaker, *Proc. Roy. Soc.* lxxxi. 21 (1908). Thus, for example, for ether at 314° absolute we have  $E=49.36$  and  $\lambda=14.19$ .

where  $D_1$  and  $D_2$  are the same for all substances at corresponding states.

The equations thus obtained may be put to various uses. It can be shown, for example, that

$$E = D_3 L \rho_c^{2/3} m^{1/3}, \quad . . . . . (104)$$

where  $D_3$  is the same for all substances at corresponding states. On comparing this equation with the equation obtained by Whittaker,

$$E = K T L, \quad . . . . . (105)$$

where  $K$  is a constant depending only on the nature of the liquid, it will appear that  $D_3 = k T/T_c$ , where  $k$  is a constant. It follows, therefore, that

$$K = \frac{k \rho_c^{2/3} m^{1/3}}{T_c},$$

which is found to agree with the facts\*.

\* R. D. Kleeman, *Phil. Mag.* xviii. 39 (1909).

## CHAPTER V.

APPLICATIONS OF THE INDETERMINATENESS OF THE NUMBER OF  
INTERNAL LATENT-HEAT AND SURFACE-TENSION EQUATIONS  
SATISFYING THE FACTS.

60. We have seen in Art. 7 that an infinite number of equations connecting the internal heat of evaporation with other quantities can be found, each of which corresponds to a certain form of the function in the law of molecular attraction. These equations can so far be found by trial only. The problem of finding them stated in strict mathematical terms is as follows: the equation for the internal heat of evaporation must fundamentally be of the form

$$L = \psi'(T, \rho_1) - \psi'(T, \rho_2), \quad . \quad . \quad . \quad . \quad . \quad (106)$$

which expresses this quantity as the difference between the values of two functions, one expressing the internal energy of a gram of substance in the liquid state at the density  $\rho_1$ , and the other the internal energy in the vaporous state at the density  $\rho_2$ . A relation exists between the quantities  $\rho_1$  and  $\rho_2$  according to thermodynamics, which may be written  $\rho_2 = \psi''(\rho_1)$ , and which we will suppose is given, or that it has been determined from the facts. By virtue of this relation the latent-heat equation may also have the form

$$L = \psi'''(T, \rho_1) \quad . \quad . \quad . \quad . \quad . \quad . \quad (107)$$

Suppose that one form of this equation representing the facts is given. The preceding equation giving the latent heat may then be written

$$\psi'''(T, \rho_1) = \psi'(T, \rho_1) - \psi'(T, \psi''(\rho_1)). \quad . \quad . \quad . \quad (108)$$

The finding of the various equations for the internal heat of evaporation then resolves itself into finding the different forms

of the function  $\psi'$  which will satisfy the foregoing equation. The method of solution of such an equation has not yet been contemplated in mathematics. The various expressions for  $L$  of a substance have therefore to be found by trial. Each expression thus obtained for a single substance may then be generalized\* in the following way to apply to all normal substances:

The law of molecular attraction given in Art. 5 furnishes the general equation

$$L = \left\{ \phi_2 \left( \frac{T}{T_c}, \frac{\rho_1}{\rho_c} \right) \cdot \rho_1^{4.3} - \phi_2 \left( \frac{T}{T_c}, \frac{\rho_2}{\rho_c} \right) \cdot \rho_2^{4.3} \right\} \frac{(\Sigma c^a)^2}{m^{7/3}} \quad . \quad . \quad (109)$$

for the internal heat of evaporation (equation 15) in which the constants are expressed in forms of the critical quantities, and atomic and numerical constants. Since the function  $\phi_2$  may have various forms, we may select one which reduces the equation to the same form in respect to  $\rho_1$ ,  $\rho_2$ , and  $T$  as an equation found by trial to represent the facts. A comparison of the coefficients of the two equations then enables us to express the coefficients in the latter equation in terms of critical quantities and numerical constants. The empirical equation can thus be given a form which applies to other substances than the one from which it was deduced.

It will be seen that the function  $\phi_2$  in equation (109), must satisfy the condition that it is the same for all substances at corresponding states. It may therefore be taken to contain other ratios besides those given, provided it retains this property. It may be noted that all ratios may be expressed as functions of the ratios

$$\frac{T}{T_c}, \frac{\rho_1}{\rho_c}, \quad \text{and} \quad \frac{\rho^2}{\rho_c}.$$

The form of the equation may also be modified by means of equations (25) and (26).

\* R. D. Kleeman, *Phil. Mag.* xx. 665 (1910); xxi. 83 (1911).

61. A number of examples of the foregoing considerations will now be given :—

(a) The internal heat of evaporation is found to be well expressed by the equation

$$L = E_1(\rho_1^2 - \rho_2^2), \quad . \quad . \quad . \quad . \quad . \quad . \quad (110)$$

where  $E_1$  is a constant depending only on the nature of the liquid. This equation was first obtained by Batschinski \* and further tested by the writer. The values of  $E_1$  over considerable ranges of temperature are given in Table XXII. for four

TABLE XXII.

n. Hexane, $C_6H_{14}$ . M. wt. 86.				
$T_1$ .	$\rho_1$ .	$\rho_2$ .	L.	$E_1$ .
273	·6770	·02268	84·68	184·8
383	·5703	·00952	64·01	196·8
443	·4913	·03472	47·41	197·3
499	·3557	·1203	21·33	190·2
506	·3040	·1658	11·76	180·9
Carbon tetrachloride, $CCl_4$ . M. wt. 151.				
273	1·6324	·02984	48·35	18·12
413	1·3450	·02481	35·56	19·65
473	1·1888	·07418	28·22	20·01
533	·9409	·2146	17·15	20·44
553	·7634	·3597	8·90	19·63
Methyl formate, $C_2H_4O_2$ . M. wt. 60.				
273	1·0032	·06821	113·2	112·6
343	·8968	·007968	92·16	114·7
403	·7860	·03344	71·95	116·6
463	·6148	·1178	41·93	115·2
483	·4857	·2188	19·58	104·2
Bromo benzene, $C_6H_5Br$ . M. wt. 57.				
303	1·4815	·04702	64·84	29·51
533	1·1310	·03427	40·82	31·91

liquids out of twenty-two examined. It will be seen that the values are practically independent of the temperature.

\* A. Batschinski, *Ann. der Physik*, xiv, 305 (1904).



On comparing equation (110) with equation (109) it will appear that

$$E_1 = h_1 \frac{(\sum \sqrt{a_w})^2}{m^{1/3} \rho_c^{2/3}} \quad . \quad . \quad . \quad . \quad . \quad (111)$$

writing  $\sqrt{a_w}$  for  $c_a$  according to Art. 18, where  $h_1$  is a numerical constant.

Table XXIII. gives the mean values of  $E_1$  obtained by means of equation (110) for a number of liquids, and the values calculated by equation (111), taking  $h_1$  equal to 2073. The agreement, it will be seen, is fairly good.

TABLE XXIII.

Name of substance.	$\rho_c$ .	$E_1$ (Equa. 110).	$E_1$ (Equa. 111).
Chlorobenzene . . . . .	·3654	71·49	66·83
Pentane . . . . .	·2323	209·4	217·7
Heptane . . . . .	·2341	185	158·6
Stannic chloride . . . . .	·7419	6·779	7·009
Ethyl oxide . . . . .	·2604	168·3	171·3
Benzene . . . . .	·3045	134·3	126·3
Iodobenzene . . . . .	·5814	17·45	16·67
Hexamethylene . . . . .	·2735	151·8	191·8
Carbon dioxide . . . . .	·464	57·37	66·43
Octano . . . . .	·2327	176·2	165·5
Carbon tetrachloride ..	·5576	19·74	17·93
Ethyl acetate . . . . .	·2993	115·3	119·8
Fluorobenzene . . . . .	·3541	81·44	82·30
Bromobenzene . . . . .	·4853	30·53	30·39
Ethyl formate . . . . .	·315	113·9	115·8

(b) Mills\* has shown that the internal heat of evaporation may be expressed by the equation

$$L = E_2(\rho_1^{1/3} - \rho_2^{1/3}), \quad . \quad . \quad . \quad . \quad . \quad (112)$$

where  $E_2$  is a constant which depends only on the nature of the liquid.

\* J. E. Mills, *Journal of Phys. Chemistry*, viii. 383 (1904).

A comparison of equation (112) with equation (109) shows that

$$E_2 = h_2 \frac{\rho_c (\Sigma \sqrt{a_w})^2}{m^{7/3}}, \quad . \quad . \quad . \quad . \quad . \quad (113)$$

where  $h_2$  is a numerical constant and  $\Sigma c_a$  is replaced by  $\Sigma \sqrt{a_w}$  as before. Table XXIV. contains the values of  $E_2$

TABLE XXIV.

Name of substance.	$E_2$ . Equat. (112).	$E_2$ . Equat. (113).	Name of substance.	$E_2$ . Equat. (112).	$E_2$ . Equat. (113).
Ether . . . . .	104.4	112.7	Fluorbenzene . . . .	85.6	97.5
Di-isobutyl . . . .	86.3	100.3	Chlorobenzene . . . .	81.2	77.3
Isopentane . . . .	105.4	119.3	Bromobenzene . . . .	56.1	56.4
n. hexane . . . .	102.8	98.7	Iodobenzene . . . . .	44.4	41.8
n. octane . . . . .	93.0	90.24	Carbon t. chloride..	44.1	52.8
Benzene . . . . .	109.5	107.6	Stannic chloride ..	26.0	26.4

calculated for a few liquids by means of this equation. Taking  $h_2=12830$  and the mean values given by Mills, a fair agreement is obtained.

(c) The equation

$$L = k_1 \frac{RT}{m} \log \frac{\rho_1}{\rho_2} \quad . \quad . \quad . \quad . \quad . \quad (114)$$

was proposed by Dieterici\* and applied by him to a few liquids, where  $R$  is the gas constant and  $k_1$  a numerical quantity. The equation has been tested by the writer† for a larger number of liquids over considerable ranges of temperature. The mean value of  $k_1$  deduced from all the reliable data is 1.75. It can be shown from equation (109) similarly as before, using also equation (26), that  $k_1$  is a constant as found from the facts.

Similarly, the constants in any other heat equation can be expressed in terms of the critical constants and other quantities.

It should be noted that the latent-heat equations con-

\* C. Dieterici, *Ann. der Physik*, xxv. 569 (1908).

† R. D. Kleeman, *Phil. Mag.* xx. 689 (1910); xxi. 83 (1911).

sidered furnish some forms of the function  $\psi'$  which are solutions of equation (108).

The agreements obtained are further evidence, it is important to notice, that *the law of molecular attraction has the general form given in Art. 5*, on which equation (109) is based. In particular, additional proof is furnished that the attraction constant of an atom is proportional to the square root of its atomic weight.

62. We have seen (Art. 7) that each of the infinite number of expressions that can be found for the internal heat of evaporation corresponds to a different law of attraction between the molecules; in other words, each of these laws can give rise to a heat of evaporation possessing the properties this quantity has in practice. It will be of interest to determine the laws of attraction corresponding to the latent-heat equations discussed in the previous Article.

This will be facilitated by obtaining first an expression for  $L$  corresponding to the general law of attraction  $K/z^n$ , where  $z$  denotes the distance of separation of the attracting molecules and  $K$  and  $n$  are constants. It will appear from the investigation in Art. 6 that the expression for the heat of evaporation is, in that case, given by an expression which is the same in form as that for the energy required to separate two molecules from the distance of separation  $z_1$  in the liquid state to that of  $z_2$  in the vaporous state. Therefore we have

$$L = K_2 \int_{z_2}^{z_1} \frac{1}{z^{n_1}} \cdot dz = K_3 \left\{ \left( \frac{\rho_1}{m} \right)^{\frac{n_1-1}{3}} - \left( \frac{\rho_2}{m} \right)^{\frac{n_1-1}{3}} \right\}, \quad (115)$$

where  $z_1 = \left( \frac{m_a}{\rho_1} \right)^{1/3}$ ,  $z_2 = \left( \frac{m_a}{\rho_2} \right)^{1/3}$ , and  $K_3$  denotes a constant depending only on the nature of the liquid and its temperature\*. On writing  $n_1=2$  we obtain Mills's equation, which therefore corresponds to an inverse square law of attraction. Mills, in fact, deduced his equation from the assumption that

\*  $m_a$  is replaced by  $m$  in the equation.

this law holds. On writing  $n_1=7$ , equation (110) is obtained, which therefore corresponds to an inverse seventh power law. When  $n_1=1$  the evaluation of the integral of the above equation gives equation (114), which is Dieterici's equation.

Thus very diverse laws of molecular attraction may represent the facts considered in the previous Article, as is to be expected from Art. 7. The assumption often made that the law of attraction can be determined from data of latent heat of evaporation has, for this reason, led to many contradictory and absurd results.

63. According to Art. 45, an infinite number of empirical equations giving the surface tension of a liquid can be found, each of which corresponds to a different law of attraction between the molecules. The constants of these equations may be expressed in terms of critical and other constants similarly as in Art. 61 in the case of empirical latent-heat equations. Equation (91) written in the form

$$\lambda = \phi_3 \left( \frac{T}{T_c}, \frac{\rho_1}{\rho_c}, \frac{\rho_2}{\rho_c} \right) \left( \frac{\rho_1 - \rho_2}{m} \right) (\Sigma c_a)^2 \quad . \quad . \quad (116)$$

is used for this purpose in the same way as equation (109) in Art. 60. It may be modified in form by means of equations (25) and (26).

(a) The surface tension of a liquid can be well expressed by the equation

$$\lambda = F_1(\rho_1 - \rho_2)^4 \quad . \quad . \quad . \quad . \quad . \quad (117)$$

obtained by the writer\*, where  $F_1$  depends only on the nature of the liquid. It agrees well with the facts except near the critical point, where the errors in the values of  $\rho_1$  and  $\rho_2$  would greatly affect the values of  $\lambda$ . Table XXV. gives for illustration the values of  $F_1$  at different temperatures for a number of liquids calculated by means of equation (117).

\* *Phil. Mag.* xxi. 99 (1911)

On comparing equations (117) and (116) it will appear that

$$F_1 = h_5 \frac{(\Sigma \sqrt{a_w})^-}{m^2 \rho_c^2} \dots \dots \dots (118)$$

on replacing  $\Sigma c_a$  by  $\Sigma \sqrt{a_w}$  as before, where  $h_5$  denotes a numerical constant. The values of  $F_1$  calculated by means

TABLE XXV.

Ethyl oxide.		Methyl formate.		Carbon tetrachloride.		Benzene.	
T°.	F <sub>1</sub> .	T°.	F <sub>1</sub> .	T°.	F <sub>1</sub> .	T°.	F <sub>1</sub> .
313	63.56	303	27.46	363	4.014	353	46.72
343	62.22	333	27.44	393	4.017	383	46.78
373	62.82	363	27.38	423	4.018	413	46.77
403	63.39	393	27.74	453	4.064	443	46.76
433	63.40	423	27.86	483	4.134	473	46.98
443	64.79	433	28.11	503	4.148	493	47.89

of this equation, taking  $h_5 = 32.96$ , and the values deduced from experimental data, are given in Table XXVI. for a

TABLE XXVI.

Name of substance.	F <sub>1</sub> (exp.).	F <sub>1</sub> (cal.).
Methyl formate . . . . .	27.53	26.93
Carbon tetrachloride . . . .	3.89	3.33
Benzene . . . . .	46.5	41.76
Ether . . . . .	62.92	68.77

number of liquids. The agreement between the two sets of values is very good. Similarly, Van der Waals's \* and Eötvös' † surface tensions may be interpreted.

An empirical formulæ for the surface tension and internal heat of evaporation may be given any form we please, provided it contain a sufficiently large number of constants, which may be determined by applying the equation to a judicious selection of values of the available data. Useful forms are

\* *Zeit. Phys. Chem.* xiii. 716 (1894). The equation is  $\lambda = C(1 - T/T_c)^D$  where C and D are constants.

† *Wied. Ann.* xxvii. 452 (1886). The equation is  $\lambda = k(\rho_1/m)^{2/3}(T_c - T)$  where k is a constant.

series of powers of  $T$ , or  $\rho$ , or of other quantities. The constants in each formulæ can be expressed in terms of the critical and other constants by expanding equations (116) and (109) in such a way that the same kind of formulæ as the empirical formulæ are obtained. Examples will be found in the papers cited.

64. We have seen in Art. 46 that the formulæ for the internal heat of evaporation and surface tension differ from each other by the factors  $\phi_1(\rho_1, \rho_2, T)$  and  $\phi_2(\rho_1, \rho_2, T)$ . The ratio  $R'$  of these factors is obtained by dividing the first of equations (88) by the first of equations (90) giving

$$R' = \frac{\phi_1(\rho_1, \rho_2, T)}{\phi_2(\rho_1, \rho_2, T)} = \frac{L}{\lambda} \quad . \quad . \quad . \quad (119)$$

This ratio may be determined from any two equations giving the internal heat of evaporation and surface tension. On substituting for  $L$  and  $\lambda$  in equation (119) from equations (117) and (110) it becomes

$$R' = \frac{2073}{32 \cdot 96} \frac{\rho_1 + \rho_2}{(\rho_1 - \rho_2)^3} \frac{\rho_c^{4/3}}{m^{1/3}}, \quad . \quad . \quad . \quad (120)$$

which expresses  $R'$  in terms of the densities of the liquid and saturated vapour. Equation (119) may now be written

$$\lambda = L \frac{32 \cdot 96}{2073} \frac{(\rho_1 - \rho_2)^3}{\rho_1 + \rho_2} \frac{m^{1/3}}{\rho_c^{1/3}} \quad . \quad . \quad . \quad (121)$$

Thus if a formula for the internal heat of evaporation is obtained, a corresponding formula for the surface tension may be obtained from the foregoing equation, and *vice versa*.

65. The pressure of the saturated vapour of a liquid is often expressed as a function of the temperature. A number of relations of an empirical nature between these quantities have been proposed. The nature of the constants in these relations can in all normal cases be determined along similar lines as laid down in Arts. 63 and 61. Equation (25) is used

in this case as the equation of reference, which may be written

$$p = \phi_s \left( \frac{\rho_1}{\rho_c}, \frac{\rho_2}{\rho_c}, T_c \right) \cdot \left( \frac{\rho_1}{m} \right)^{7/3} (\Sigma c_a)^2. \quad (122)$$

For example, one of the formulæ that has been proposed \* is

$$\log p = A - \frac{B}{T}, \quad (123)$$

where A and B are constants depending on the nature of the liquid. On comparing this equation with the foregoing equation given a similar form, we obtain

$$A = \log \left\{ c' \left( \frac{\rho_c}{m} \right)^{7/3} (\Sigma c_a)^2 \right\}$$

$$B = c'' T_c$$

where  $c'$  and  $c''$  are numerical constants. Similarly, an empirical equation of state applying to a substance in any given state may be dealt with.

66. It was shown in Art. 8 that equations giving the relation between the quantities  $\rho_1$ ,  $\rho_2$ , and  $T$  of a liquid and its saturated vapour may be obtained by the fundamental method of equating the various expressions for the internal heat of evaporation which can be found according to Art. 7. Only two of these equations are independent according to Art. 8, but any two may be selected, as is convenient. Two equations of this nature will be pointed out and discussed in this Article.

Thus on equating the values of  $L$  given by equations (114), (112), and (110) we obtain the equations †

$$B_1 (\rho_1^{1/3} - \rho_2^{1/3}) = T \log \frac{\rho_1}{\rho_2}. \quad (124)$$

$$B_2 (\rho_1^{1/3} - \rho_2^{1/3}) = \rho_1^2 - \rho_2^2. \quad (125)$$

where  $B_2 = \frac{E_2}{E_1}$  and  $B_1 = \frac{E_2 m}{k_1 h}$ .

The most convenient expressions for  $B_1$  and  $B_2$  are obtained

\* Dupre, *Théorie mécanique de la chaleur*. (Paris: Gauthier Villars, 1869, p. 96.)

† R. D. Kleeman, *Phil. Mag.* xxi. 325 (1911).

on writing  $\rho_2 = x\rho_1$ , and evaluating the limiting forms the equations assume on being applied to the critical point which corresponds to  $x=1$ . This operation gives  $B_1 = \frac{3T_c}{\rho_c^{2/3}}$  and  $B_2 = 6\rho_c^{5/3}$ , and hence the equations may be written

$$\frac{3T_c}{\rho_c^{1/3}}(\rho_1^{1/3} - \rho_2^{1/3}) = T \log \frac{\rho_1}{\rho_2} \quad . \quad . \quad . \quad (126)$$

$$6\rho_c^{5/3}(\rho_1^{1/3} - \rho_2^{1/3}) = \rho_1^2 - \rho_2^2 \quad . \quad . \quad . \quad (127)$$

It may be pointed out that, on equating the former expressions for  $B_1$  and  $B_2$  with the latter expressions, relations between the numerical coefficients they contain are obtained.

An application of equation (124) to the facts shows that  $B_1$  is remarkably constant over wide ranges of temperature (as should be the case), which is shown for a few liquids in Table XXVII. The mean values of  $B_1$  for a number of

TABLE XXVII.

Pentane.		Stannic chloride.		Ethyl acetate.		Fluorbenzene.	
T°.	$\frac{10^4}{B_1}$	T°.	$\frac{10^4}{B_1}$	T°.	$\frac{10^4}{B_1}$	T°.	$\frac{10^4}{B_1}$
273	4.21	373	4.96	273	3.81	273	3.89
353	4.29	433	5.02	403	4.13	393	4.14
413	4.27	493	5.01	463	4.15	473	4.13
469	4.31	553	4.99	522	4.27	553	4.15

liquids and the corresponding values of  $\frac{3T_c}{\rho_c^{1/3}}$  are given in Table XXVIII.

From equations (126) and (127) the equation

$$B_2(\rho_1^2 - \rho_2^2) = T \log \frac{\rho_1}{\rho_2} \quad . \quad . \quad . \quad (128)$$

may be deduced, where  $B_3 = \frac{T_c}{2\rho_c^2}$ . The mean values of  $B_3$  at different temperatures for a number of substances and the corresponding values of  $T_c/2\rho_c^2$  are given in Table XXVIII. A good agreement between the two sets of values is obtained.

The three equations (128), (127), and (126) (two of which



are independent), which express relations between the quantities  $\rho_1$ ,  $\rho_2$ , and  $T$  will be found very convenient in various considerations connected with liquids in contact with their saturated vapours.

67. If the quantities  $\rho_1$ ,  $\rho_2$ , and  $T$  are expressed in terms of their critical values by means of the equations  $\rho_1 = e_1 \rho_c$ ,  $\rho_2 = e_2 \rho_c$ , and  $T = e_3 T_c$  given in Art. 10 the equations (126) and (127) assume the form

$$3(e_1^{1/3} - e_2^{1/3}) = e_3 \log \frac{e_1}{e_2} \quad . \quad . \quad . \quad . \quad . \quad (129)$$

$$6(e_1^{1/3} - e_2^{1/3}) = e_1^2 - e_2^2 \quad . \quad . \quad . \quad . \quad . \quad (130)$$

TABLE XXVIII.

Name of substance.	$\frac{B_1}{10^4}$	$\frac{3T_c}{10^3 \rho_c^{1/3}}$	$B_2$	$\frac{T_c}{2\rho_c}$	$\psi(T), \frac{\rho_c^{1/3}}{3}(3 - \log \rho_c)$	
Ethyl oxide . . . . .	2.24	2.20	3471	3445	.930	.931
Pentane . . . . .	2.33	2.29	4493	4468	.912	.916
Stannic chloride ..	2.00	1.96	545.8	537.5	1.08	1.29
Octane . . . . .	2.88	2.78	5511	5255	.916	.914
Benzene . . . . .	2.54	2.51	3125	3031	.950	.939
Heptane . . . . .	2.72	2.63	5173	4924	.914	.915
Iodobenzene . . . . .	2.64	2.59	1067	1066	1.08	1.22
Bromobenzene ....	2.60	2.56	1430	1423	1.03	1.23
Hexane . . . . .	2.53	2.47	4822	4631	1.07	.914
Carbon tetrachloride	2.05	2.03	930	894	1.02	1.27
Di-isobutyl . . . . .	2.76	2.64	5174	4857	.918	.915
Ethyl acetate ....	2.40	2.35	2853	2916	.952	.938
Chlorobenzene ....	2.70	2.66	2416	2573	.983	.977
Carbon dioxide ....	1.20	1.43	743.2	706.5	.991	.972
Acetone . . . . .	2.51	—	—	—	.953	—
Chloroform . . . . .	2.02	—	—	—	1.09	—
Fluorobenzene ....	2.42	2.37	2305	2231	.972	.953
Hexamethylene ..	2.61	2.54	3825	3794	1.23	.929
Sulphur dioxide ..	1.61	—	—	—	1.05	—
Ethyl formate ....	2.13	2.23	2515	2535	1.00	.942

They express the relation of corresponding states, since each of the quantities  $e_1$ ,  $e_2$ , and  $e_3$  is determined if one of them is given.

68. It was pointed out in Art. 9 that the equations obtained by equating the expressions for  $L$  given by the different latent-heat equations that can be obtained according to Art. 7 could be used to calculate the critical quantities from any convenient data. Thus, for example, from equation (125) and the equation  $B_2 = 6\rho_c^{5/3}$  and  $B_1 = \frac{3T_c}{\rho_c^{2/3}}$  we have

$$\rho_c = \left\{ \frac{\rho_1^2 - \rho_2^2}{6(\rho_1^{1/3} - \rho_2^{1/3})} \right\}^{3/5} \dots \dots \dots (131)$$

and

$$T_c = \frac{B_1}{3} \rho_c^{2/3}, \dots \dots \dots (132)$$

where the value of  $B_1$  is calculated by equation (124). The value of  $p_c$  is given by the equation

$$p_c = \frac{\rho_c RT}{3 \cdot 7 m} \dots \dots \dots (133)$$

given in Art. 15.

The values of  $\rho_c$  have been calculated by means of equation (131) for a number of substances and are contained in Table XXIX., which also contains the data used. They agree very well with the experimental values, which were taken from Landolt and Bornstein's Tables, Third Edition.

The Table also contains the values of  $T_c$  calculated by means of equation (132). The values of  $\rho_c$  used in the calculations are the calculated values given in the Table, the values of  $B_1$  being obtained by means of equation (124) from the same data. The agreement between the calculated and the experimental values of  $T_c$  would be still better if the experimental values of  $\rho_c$  instead of the calculated had been used in the calculations.

69. Two equations may be obtained from equations (126) and (127) by elimination, one of which expresses  $\rho_1$  and the other  $\rho_2$  in terms of  $T$ . The process is, however, beset by

algebraical difficulties, as will be seen from inspection. But the desired result may be obtained along different lines.

An equation of the form

$$\phi_1(\rho_1, T) = \phi_1(\rho_2, T),$$

applying to a liquid in contact with its saturated vapour, may be written in the form of two equations, thus:

$$\phi_1(\rho_1, T) = \psi_1(T)$$

and

$$\phi_1(\rho_2, T) = \psi_1(T),$$

where  $\psi_1(T)$  is an appropriate function of  $T$ . The quantities  $\rho_1$  and  $\rho_2$  are now expressed as functions of  $T$ . The function

TABLE XXIX.

Name of liquid.	$T^\circ$ .	$\rho_1$ .	$\rho_2$ .	$\rho_c$ (exp.).	$\rho_c$ (cal.).	$T_c$ (cal.).	$T_c$ (exp.).
Ethyl oxide . . . . .	393	·7135	·00187	2604	·2661	467·4	484·8
Octane . . . . .	393	·6168	·0033	·2327	·2243	569·2	592·4
Ethyl propionate ..	383	·7823	·004739	·2860	·3011	545·4	580·1
Pentane . . . . .	313	·6062	·00339	·2323	·2505	470·0	489·8
Benzene . . . . .	353	·8145	·002722	·3045	·3071	561·5	569·4
Carbon tetrachloride.	373	1·4343	·01026	·5576	·5563	556·1	555·0
Iodobenzene . . . .	473	1·7079	·04400	·5814	·5755	721	729·3
Bromobenzene . . . .	433	1·2994	·005255	·4853	·4919	670	684·4
Ethyl acetate . . . . .	363	·8112	·004673	·2993	·3076	522·5	550·3
Fluorobenzene . . . . .	353	·9496	·002885	·3541	·3559	559·5	575·0
Carbon dioxide . . . .	363	·9560	·0725	·464	·4606	304·3	307·0
Hexamethylene . . . .	363	·7106	·003759	·2735	·2721	553	558·0
Chlorobenzene . . . .	413	·9723	·004316	·3654	·3695	633	646·8
Methyl formate . . . .	303	·9598	·002225	·3489	·3567	487	477·7

$\psi_1$  is therefore an important one, and may therefore possess important and interesting properties. Its nature must be found by trial.

If equation (126), Art. 66, is split into equations in this way the equations

$$\rho_1^{1/3} - \frac{\rho_c^{1/3} T}{3T_c} \log \rho_1 = \psi_1(T) \quad . \quad . \quad . \quad (134)$$

and

$$\rho_2^{1/3} - \frac{\rho_c^{1/3} T}{3T_c} \log \rho_2 = \psi_1(T) \quad . \quad . \quad . \quad (135)$$

are obtained. On applying these equations to the facts, it is found that the function  $\psi_1$  is a constant which is independent of the temperature and varies little with the nature of the liquid. This is shown for several liquids in Table XXX., the values of  $\psi_1(T)$  being calculated by means of equation (134).

TABLE XXX.

Carbon tetrachloride.		Fluorbenzene.		Hexane.		Iodobenzene.	
T.	$\psi_1(T).$	T.	$\psi_1(T).$	T.	$\psi_1(T).$	T.	$\psi_1(T).$
373	1.05	353	.995	343	1.12	473	1.17
433	1.03	413	.976	403	1.09	643	1.05
493	1.02	473	.967	463	1.05	<hr/>	
553	1.00	553	.952	506	1.00	Sulphur dioxide.	
						283	1.06
						403	1.00

The nature of the constant can be determined by applying either of the equations to the critical point. The equations accordingly assume the forms

$$\rho_1^{1/3} - \frac{\rho_c^{1/3} T}{3T_c} \log \rho_1 = \frac{\rho_c^{1/3}}{3} (3 - \log \rho_c). \quad \dots \quad (136)$$

and

$$\rho_2^{1/3} - \frac{\rho_c^{1/3} T}{3T_c} \log \rho_2 = \frac{\rho_c^{1/3}}{3} (3 - \log \rho_c). \quad \dots \quad (137)$$

The mean values of  $\psi_1(T)$  calculated by means of equation (134) for a number of liquids and the corresponding values of  $\frac{\rho_c^{1/3}}{3} (3 - \log \rho_c)$  are given in Table XXVIII. Another application of the principle used in this Article will now be given.

70. On comparing equations (126) and (114) it will be seen that the latent-heat equation (114) may be written in the form

$$L = \frac{5.25RT_c}{m\rho_c^{1/3}} (\rho_1^{1/3} - \rho_2^{1/3}) \quad \dots \quad (138)$$

Substituting the value of  $L$  given by this equation in Clapeyron's thermodynamical equation (5) and splitting the

equation into two in the same way as indicated in the previous Article, we obtain the equations

$$\frac{dp}{dT} \frac{T}{\rho_1} - \frac{p}{\rho_1} = \frac{5 \cdot 25 RT_c}{m \rho_c^{1/3}} \rho_1^{1/3} + \psi_2(T) \quad . \quad . \quad . \quad (139)$$

and

$$\frac{dp}{dT} \frac{T}{\rho_2} - \frac{p}{\rho_2} = \frac{5 \cdot 25 RT_c}{m \rho_c^{1/3}} \rho_2^{1/3} + \psi_2(T) \quad . \quad . \quad . \quad (140)$$

The application of these equations to the facts shows that  $\psi_2(T)$  is independent of the temperature.

The foregoing equations can be expressed as a single equation which differs in form from the original equation.

Thus on eliminating  $T \frac{dp}{dT} - p$  we obtain

$$C(\rho_1^{4/3} - \rho_2^{4/3}) = \rho_1 - \rho_2, \quad . \quad . \quad . \quad (141)$$

where  $C = \frac{5 \cdot 25 RT_c}{m \rho_c^{1/3} \cdot \psi_2(T)}$ . On applying this equation to the facts it is found that  $C$  is independent of the temperature, as we should expect from the foregoing result. An expression for  $C$  is obtained on finding its limiting value when the preceding equation is applied to the critical point. In this way it is found that  $C = \frac{2}{3} \rho_c^{1/3}$ . On comparing the two expressions obtained for  $C$  it will be seen that  $\psi_2(T) = \frac{7 RT_c}{m}$ , which agrees with the facts\*.

71. Any empirical formula that connects the physical properties of a number of normal substances may be used to detect whether polymerization of the molecules exists in the case of other substances. This state would be indicated by the formula not fitting the facts. Such formulæ usually contain the symbol for the molecular weight. Attempts to deduce the extent of polymerization have been made by finding the factor of the molecular weight which makes the formula fit the facts. But this can give rise to quite reliable results only under certain conditions (usually not recognized)

\* *Loco. cit.*

which are not realized in practice. If the constants of the formula used consist only of the molecular weight and numerical constants, the extent of polymerization could be exactly determined in this way in the case of a liquid each of whose molecules is polymerized to the same extent at the temperature at which the formula is applied. For the liquid is then really a normal liquid, if we assign to each molecule its proper molecular weight. If the molecules are polymerized to different extents an average molecular weight would be obtained in this way, but this is not the exact average molecular weight, because the formula, *a priori*, applies to normal liquids only, and therefore does not necessarily apply to mixtures.

In practice, however, these formulæ contain other constants depending on the nature of the liquid besides the molecular weight, such as the critical constant, etc. In that case a formula would give reliable results only if all the molecules are polymerized to the same extent at *all temperatures* up to the critical point. For if the extent of polymerization of a liquid varies with the temperature, the values of the critical quantities would not be the same as if the nature of the molecules did not vary in this way. This follows from experiments on the critical quantities of mixtures. Therefore if the formula is applied to such a liquid at a temperature for which each molecule is polymerized to the same extent, the values substituted for the critical constants in the formula do not correspond to the degree of polymerization. The correct polymerization factor will therefore not be given by the formula. If the molecules are polymerized to different extents at the temperature that the formula is applied, then an average polymerization factor is obtained which is not correct for the same reason, and another reason which was stated in the preceding paragraph.

Thus we see that the various formulæ that may be used to detect the existence of polymerization of the molecules of

a liquid will not give equally pronounced and equally reliable results. The degree of polymerization obtained for a liquid will accordingly depend on the formula used for its determination, and in no case is the result likely to strictly represent the facts. This explains why such conflicting results have been obtained in the determination of the degrees of polymerization by various formulæ. It will be of interest to consider some of these formulæ in this connexion more closely.

The surface-tension equation given by Eötvös has been mostly used for investigating the polymerization of liquids. But each of the equations (127), (126), (121), (117), (114), (110), (91), (26), (25), (23), and others may evidently be used for the same purpose. Sometimes one equation is more convenient to apply than another. But *a priori* there is no reason why one should give better results than the others.

Using Eötvös' equation\*, Ramsay and Shields† found that water, acetic acid, and the alcohols are more or less polymerized. This may be verified by applying the above-mentioned equations to these liquids.

A few additional important cases of polymerization may be pointed out here. By means of equation (114) it can be shown that  $\text{NH}_3$  is considerably polymerized in the liquid state. The constant  $k_1$ , instead of being equal to 1.75, varies from 2.6 to 3.9 as the temperature is varied from  $-10^\circ$  to  $40^\circ$  C. It will also be found that the critical quantities of oxygen do not fit in with equation (25), and liquid oxygen is therefore to a certain extent polymerized. Mercury is usually supposed to be polymerized. It will, however, be found that if the internal heat of evaporation is calculated by means of Clapyron's equation and substituted in equation (110) the value of  $E_v$  is not constant, but increases rapidly with the temperature, showing that mercury is to a certain extent polymerized.

\* Reference on p. 103.

† Ramsay & Shields, *Zeitsch. phys. Chem.* xii. 433 (1893): Ramsay & Aston, *ibid.* xv. 98 (1894).

72. A liquid may consist of: (a) molecules whose molecular weight is that indicated by the chemical formula; (b) molecules each of which is polymerized to the same degree which depends on the temperature; (c) a mixture of molecules polymerized in different degrees, whose proportion depend on the temperature. The formulæ discussed in the previous Article do not distinguish between the last two cases. It will therefore be of importance to develop one that does\*.

According to equation (117) in Art. 63 the surface tension of a liquid is given by

$$\lambda = \rho_1^4 \frac{32 \cdot 96}{m^2 \rho_c^2} (\Sigma \sqrt{a_w})^2$$

when the density  $\rho_1$  of the liquid is large in comparison with that of its surrounding vapour. Since  $\frac{m}{\rho_c}$  according to Art. 16 is approximately proportional to  $\Sigma \sqrt{a_w}$  we may write  $\frac{m}{\rho_c} = 10 \Sigma \sqrt{a_w}$ . Hence the foregoing equation may be written

$$\frac{\lambda}{\rho_1^4} = 3296 \left( \frac{\Sigma \sqrt{a_w}}{m} \right)^4 \quad . \quad . \quad . \quad . \quad . \quad (142)$$

This equation holds independently of the extent of polymerization, provided the molecules are all polymerized to the *same extent*, in which case  $m$  and  $\Sigma \sqrt{a_w}$  have the same polymeriza-

TABLE XXXI.

Name of liquid.	$\frac{\lambda}{\rho_1^4}$ .	$3296 \left( \frac{\Sigma \sqrt{a_w}}{m} \right)^4$ .
Methyl formate .....	27.53	32.6
Carbon tetrachloride .....	3.99	3.25
Benzene .....	46.5	45.66
Ether .....	62.92	66.11

tion factor. The result of an application of this equation to four liquids, which are known not to be polymerized, is given in Table XXXI. It contains the values of the right- and

\* R. D. Kleoman, *Proc. Camb. Phil. Soc.* xvii, (1) 149 (1913).



left-hand sides of the equation for these liquids, which, it will be seen, agree fairly well with one another, as we would expect.

Since equation (142) holds independently of the temperature and the values of the critical quantities, it can be easily applied to various experimental data. We may, for example, use it to investigate the nature of the polymerization of fused metals and salts. A few of the results of such an investigation are, for example, given in Table XXXII. It will be seen that in most cases the value of  $\lambda/\rho_1^4$  differs very considerably from that of  $3296\left(\frac{\sum\sqrt{a_w}}{m}\right)^4$ , indicating that these fused substances consist of *a mixture of molecules polymerized in different extents*. This

TABLE XXXII.

Symbol of substance.	$\lambda$ .	$\rho_1$ .	$\frac{\lambda}{\rho_1^4}$ .	$3296\left(\frac{\sum\sqrt{a_w}}{m}\right)^4$ .
Pd. ....	1339	11.4	.07920	.2935
Pt. ....	1658	21.32	.008024	.08670
Hg. ....	435.6	13.55	.01293	.08241
Se. ....	70.4	4.26	.2138	.5286

was also shown to hold for the fused substances Ag, Bi, Zn, Sb, Pb, Fe, Au, K, Cu, Na, KBr,  $K_2CO_2$ , KCl, LiCl,  $LiCO_2$ , NaBr,  $NaCO_3$ , NaCl,  $Na_2SO_4$ , and AgBr. We would, of course, expect from Art. 17 that the molecular weight of these substances is not that indicated by their chemical formula. But this investigation gives additional information. It was also found that in the case of each of the four substances S, Sn, Cd, and P in the fused state each molecule is polymerized to the same extent.

In the next chapter the determination of the law of molecular attraction from the equation of state of a substance will be considered in detail.

## CHAPTER VI.

THE LAW OF ATTRACTION DEDUCED FROM THE EQUATION OF STATE,  
THE EFFECT OF THE MOLECULAR FORCES ON THE VELOCITY OF  
TRANSLATION OF THE MOLECULES, AND PROPERTIES OF  
MATTER EVENLY DISTRIBUTED IN SPACE.

73. The use of the equation of state of a substance in the determination of the law of molecular attraction will now be considered. This equation in its most general form is

$$p + P_n = P_e, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (143)$$

where  $p$  denotes the external pressure exerted upon the substances,  $P_n$  the intrinsic pressure or pressure of contraction due to the attraction of the molecules upon each other, and  $P_e$  the expansion pressure tending to expand the substance due to the motion of translation of the molecules. The quantities  $P_n$  and  $P_e$  are evidently functions of the absolute temperature  $T$  and the volume  $v$  of a gram of the substance. If the form of the function  $P_e$  were known the form of the function  $P_n$  could be determined by applying the equation of state to a set of facts, or *vice versa*. The law of attraction could then definitely be determined from the function  $P_n$  according to the results of Chapter III. But the exact form of  $P_e$  is at present not known independently of  $P_n$ , and the equation of state cannot therefore be used in this way.

It is of importance to point out here that the functions  $P_n$  and  $P_e$  cannot be determined simultaneously by applying the equation of state to the facts. Thus if  $\phi_1(v, T)$  and  $\phi_2(v, T)$  are proposed expressions for  $P_n$  and  $P_e$  which on being substituted in equation (143) satisfy the facts, the equation will evidently also satisfy the facts if the expressions  $\phi_1(v, T) + \psi(v, T)$

and  $\phi_2(v,T) + \psi(v,T)$  are assumed for  $P_n$  and  $P_v$ , where  $\psi(v,T)$  may have any form whatever.

74. It may be pointed out here in passing that the term  $a/v_2$  for  $P_n$  in van der Waals's equation of state corresponds to an inverse fourth power law of molecular attraction. Now we have seen in Art. 36 that, as a first rough approximation, the attraction between two molecules varies inversely as the fifth power of their distance of separation. In passing from the fourth to the fifth power law the constant of attraction will not be greatly changed proportionally for the various substances. We would therefore expect that according to Art. 18 van der Waals's constant  $a$  should be roughly additive and proportional to  $\Sigma \sqrt{a_w}$ . This will be found to be the case.

75. The complete form of the law of molecular attraction may be obtained \* from the equation of state of a normal substance by means of equation (48). A form of the law will first be obtained expressing the pressure of a substance in the form of the series

$$p = \frac{RT}{mv} \cdot \psi_1(v) + p_c \Sigma A_n \left( \frac{v_c}{v} \right)^n, \quad . . . . (144)$$

where  $\psi_1(v)$  is a function of  $v$ ,  $A_n$  a function of the temperature, and  $n$  a constant greater than unity. On substituting this expression for  $p$  in equation (48) we obtain

$$U_c = p_c \Sigma \left\{ T \left( \frac{\partial A_n}{\partial T} \right)_v - A_n \right\} \frac{v_c^n}{(n-1)v^{n-1}}, \quad . . (145)$$

where  $U_c$  is expressed in ergs when  $p_c$  is expressed in dynes.

From this expression of  $U_c$  an expression for the law of molecular attraction may be obtained. We have seen in Art. 25 that if the attraction between two molecules separated a distance  $z$  is  $\frac{K_z}{z^n}$  the energy  $U_z$  necessary to separate the

\* R. D. Kleeman, not previously published.

molecules of a gram of a substance an infinite distance from one another is given by

$$U_s = \frac{6.32}{s-1} \left( \frac{1}{vm_a} \right)^{\frac{s-1}{3}} \frac{K_s}{m_a}.$$

This general expression for  $U_s$  corresponds to the typical expressions of the series of  $U_c$  given in equation (145), if we write  $s=3n-2$ , which renders the factor involving  $v$  the same in the two expressions. On equating them we obtain

$$\frac{6.32}{3(n-1)} \left( \frac{1}{vm_a} \right)^{n-1} K_s = p_c \left\{ T \left( \frac{\partial A_n}{\partial T} \right)_v - A_n \right\} \frac{v_c^n}{(n-1)v^{n-1}} \quad (146)$$

From this equation a general expression for  $K_s$  may be obtained which is

$$K_s = \frac{p_c v_c^n m_a^n}{2.11} \left\{ T \left( \frac{\partial A_n}{\partial T} \right)_v - A_n \right\} \quad (147)$$

The law of attraction is therefore given by

$$\Sigma \frac{K_s}{z^s} = \frac{p_c}{2.11} \Sigma \frac{v_c^n m_a^n}{z^{3n-2}} \left\{ T \left( \frac{\partial A_n}{\partial T} \right)_v - A_n \right\}, \quad (148)$$

where  $s=3n-2$ .

The law may also be written

$$\frac{116.8 \times 10^6}{2.11} \frac{(\Sigma c_a)^2}{(v_c m)^{7/3}} \Sigma \frac{(v_c m_a)^n}{z^{3n-2}} \left\{ T \left( \frac{\partial A_n}{\partial T} \right)_v - A_n \right\} \quad (b)$$

by means of the equation

$$p_c = \frac{116.8 \times 10^6}{(v_c m)^{7/3}} (\Sigma c_a)^2, \quad (149)$$

which expresses  $p_c$  in dynes, and which is obtained from Art. 13, taking into account that  $v_c \rho_c = 1$ . This expression involves the attraction constant  $\Sigma c_a$  of a molecule.

76. The law of attraction (148), which is in the form of an infinite series, may be put into a form corresponding to any given equation of state, without expanding it in series. The law may evidently be written

$$\frac{p_c z^2}{2 \cdot 11} \left\{ T \left[ \frac{T}{\partial T} \left\{ \Sigma \left( \frac{v_c m_a}{z^3} \right)^n A_n \right\} - \Sigma \left( \frac{v_c m_a}{z^3} \right)^n A_n \right] \right\}.$$

If the equation of state is expressed in the general form

$$\frac{p}{p_c} = \psi \left( \frac{v_c}{v}, \frac{T}{T_c} \right)$$

it follows from this equation and equation (144) that

$$\Sigma A_n \left( \frac{v_c}{v} \right)^n = \psi \left( \frac{v_c}{v}, \frac{T}{T_c} \right) - \frac{RT}{p_c m v} \psi_1(v).$$

On substituting  $m_a/z^3$  for  $1/v$  in the equation, where  $z$  denotes the least distance of molecular separation and hence  $m_a/z^3$  the density, it becomes

$$\Sigma A_n \left( \frac{v_c m_a}{z^3} \right)^n = \psi \left( \frac{v_c m_a}{z^3}, \frac{T}{T_c} \right) - \frac{RT m_a}{p_c z^3 m} \cdot \psi_1(v).$$

By means of this equation the series in the law (148) may be eliminated, giving the law the form

$$\frac{p_c z^2}{2 \cdot 11} \left\{ T \left[ \frac{\partial}{\partial T} \psi \left( \frac{v_c m_a}{z^3}, \frac{T}{T_c} \right) \right] - \psi \left( \frac{v_c m_a}{z^3}, \frac{T}{T_c} \right) \right\} \quad \dots (c)$$

*Thus an expression for the law of force between two molecules in a substance separated by the minimum distance  $z$  of a molecular separation is obtained corresponding to any given empirical equation of state.*

It may be noted that if  $z$ , or the volume, of the substance is kept constant the attraction will vary with the temperature.

Consider, for example, the equation of state

$$p = \frac{RT}{v-b} e^{-\frac{c}{v(T+d)^2}}, \quad \dots (150)$$

which is a modified form of Dieterici's equation, where  $b$ ,  $c$ ,  $d$  are constants depending on the nature of the substance. The corresponding law of attraction is

$$\frac{z^2 p_c R T^2 m_a^2 c e^{-\frac{c m_a}{z^3(T+d)^2}}}{2 \cdot 11 z^3 (z^3 - b m_a) (T+d)^3} \quad \dots (d)$$



$M_c$  becomes a constant  $M_{sc}$ , and then substituting for  $p_c$  from it in the form (e) of the law it becomes

$$M_{sc}^2 \left( \frac{1}{m_a v_c} \right)^{s/3} ZC, \quad . . . . . (g)$$

If  $v_c$  is eliminated by means of the equation  $v = r_2 v_c$  (Art. 10) and  $v$  then eliminated by means of the equation  $z^3 = m_a v$ , the law assumes the form

$$M_{sc}^2 r_2^{s/3} \frac{ZC}{z^s}, \quad . . . . . (h)$$

where  $M_{sc}^2 r_2^{s/3} Z$  is the same for all substances at corresponding states. This investigation shows that *the law of attraction must have the form (h) according to thermodynamics and the relation of corresponding states*, which are involved in the deduction of equation (151) and the law (g).

The value of  $s$  and the nature of the constant  $C$  are not determined by this investigation. They can therefore be determined only from the actual values of some of the quantities involving molecular attraction. Thus if the law (h) is used to obtain a formula for the internal heat of evaporation  $L$ , following the investigation in Art. 11, we obtain

$$L = A_4 \left( \frac{1}{v m_n} \right)^{\frac{s-1}{3}} \frac{C}{m_a}, \quad . . . . . (152)$$

where  $A_4$  is the same for all substances at corresponding states. It follows from the investigation in Art. 11 that an application of this equation to the facts would show that *if  $s$  is taken equal to 5 the constant  $C$  becomes the square of an atomic additive quantity denoted by  $(\Sigma c_a)^2$* . This is therefore likely to be the correct value that should be assumed for  $s$ , since the law has then a form applying to all normal substances.

The constants of the law of molecular forces then consist of absolute constants, the critical constants, and  $\Sigma c_a$ .

79: The constants of the equation of state of a substance, which consist of absolute constants and the critical constants,

are determined (in part at least) by certain conditions which the equation has to satisfy. Hence these conditions also in part determine the nature of the law of molecular attraction, and it will be of interest therefore to present them here. At the critical point according to thermodynamics

$$p_c = \psi(v_c, T_c), \quad . \quad . \quad . \quad . \quad . \quad . \quad (153)$$

$$\left(\frac{\partial p}{\partial v}\right)_T = 0, \quad . \quad . \quad . \quad . \quad . \quad . \quad (154)$$

$$\left(\frac{\partial^2 p}{\partial v^2}\right)_T = 0. \quad . \quad . \quad . \quad . \quad . \quad . \quad (155)$$

Another equation may be obtained\* from Clapeyron's equation which at the critical point may be written

$$\frac{U_2 - U_1}{v_2 - v_1} = \frac{dU}{dv} = T \frac{dp}{dv} - p, \quad . \quad . \quad . \quad . \quad . \quad (156)$$

where  $u$  denotes the internal energy of the substance.

Now

$$\frac{dU}{dv} = \left(\frac{\partial U}{\partial T}\right)_v \frac{dT}{dv} + \left(\frac{\partial U}{\partial v}\right)_T,$$

and since  $dT/dv=0$  at the critical point according to thermodynamics

$$\frac{dU}{dv} = \left(\frac{\partial U}{\partial v}\right)_T.$$

Equation (156) may therefore be written

$$\left(\frac{\partial p}{\partial T}\right)_v = \frac{dp}{dT} = \frac{7.5 p_c}{T_c}, \quad . \quad . \quad . \quad . \quad . \quad (157)$$

by means of this equation and equations (47) and (9), and is one of the equations the equation of state has to satisfy.

The equation of state must also satisfy a number of relations holding at any temperature  $T$ †. On considering thermodynamically the evaporation of a liquid we obtain the well-known equation

$$p(v_2 - v_1) = \int_{v_1}^{v_2} p \cdot dv, \quad . \quad . \quad . \quad . \quad . \quad (158)$$

\* R. D. Kleeman, *Phil. Mag.* xxiv. 391 (1912).

† *Loco. cit.*



and directly from the equation of state the equation

$$p = \psi(v_1, T) = \psi(v_2, T), \quad . . . . . (159)$$

where  $v_1$  and  $v_2$  denote the volumes of a gram of vapour in the liquid and vaporous state respectively. From Clapeyron's equation

$$L = (v_2 - v_1) \left\{ T \frac{dp}{dT} - p \right\} \quad . . . . . (160)$$

and the equation

$$L = \int_{v_1}^{v_2} \left\{ T \left( \frac{\partial p}{\partial T} \right)_v - p \right\} \partial v, \quad . . . . . (161)$$

obtained by integrating equation (47), we obtain

$$\int_{v_1}^{v_2} \left( \frac{\partial p}{\partial T} \right)_v \partial v = (v_2 - v_1) \frac{dp}{dT} \quad . . . . . (162)$$

by the help of equation (158). From equations (162), (159), and (158) we may eliminate three of the quantities  $p$ ,  $v_1$ ,  $v_2$ , and  $T$  giving an equation containing one variable only and constants. The equation must accordingly vanish with respect to this variable, and the coefficients of the various terms in the equation are therefore each equal to zero. This gives a number of equations expressing relations between the coefficients of the equation of state.

The equation of state must also satisfy the condition that when  $T=0$  we have  $p=0$ .

80. The relation of corresponding states which has often figured in previous investigations, and which is connected with the law of molecular attraction, is intimately connected with the equations given in the previous article. Meslin \* has investigated the general conditions under which this relation is the outcome of these equations. The equation of state of a substance in its most general form is

$$\psi(p, T, v, c_1, c_2, \dots) = 0, \quad . . . . . (163)$$

\* Meslin, *Compt. Rend.* cxvi. 135 (1893).

where  $c_1, c_2, \dots$ , denote constants depending only on the nature of the substance. If the supposition is made that the various equations which the equation of state has to satisfy are equal to the number of the constants  $c_1, c_2, \dots$ , these constants may be eliminated giving an equation of the form

$$\psi_2(p, v, T, p_c, v_c, T_c) = 0. \quad (164)$$

This equation contains the critical quantities  $p_c, v_c, T_c$ , since some of the foregoing equations refer to the critical point. The equation must be independent of the nature of the units chosen, and therefore be of the form

$$\psi_3\left(\frac{p}{p_c}, \frac{v}{v_c}, \frac{T}{T_c}\right) = 0. \quad (165)$$

Now if in addition we make the supposition that the functional form of  $\psi_3$  is the same for all substances, the relation of corresponding state immediately follows from the foregoing equation.

If the relation rests upon the foregoing suppositions, as is highly likely, and which will be taken to be the case, it should be an exact relation, and therefore agree with the facts within the experimental error of the quantities involved. But the deviations from the relation are greater than that, which would indicate that dissociation and polymerization exist in all substances in different degrees, which would cause the function  $\psi_3$  not to be exactly the same for all substances.

It may be noted that van der Waals deduced the relation of corresponding states by applying to his equation of state the two equations (155) and (154), which hold at the critical point. This equation contains two constants only depending on the nature of the substance. But evidently, according to the investigation in the preceding Article, the equation of state should contain more constants than that, since the number of equations of condition is greater than two.

It may also be recalled that it follows from the

investigation in Arts. 8 and 10 that the relation of corresponding states may be deduced from the law of molecular attraction given in Art. 5, assuming that its form is correct. It is not impossible that this is the true basis of the relation.

81. The equations in Art. 79 may now be shown to express relations between the absolute constants of the equation of state, on account of the relation of corresponding state. Thus if the expression for  $p$  given by the general equation of state (165) is substituted in the equations (157), (155), and (154), which apply to the critical point, equations will be obtained devoid of the critical quantities, and which therefore express relations between the absolute constants of the equation of state. This also holds for the equation  $p=0$  referring to the absolute zero of temperature.

On eliminating  $p$  from equations (162), (159), and (158), three equations involving the ratios  $v_1/v_c$ ,  $v_2/v_c$ , and  $T/T_c$  will be obtained, remembering that equations (159) must conform in form to equation (165). The elimination of two of these ratios gives an equation involving one ratio containing an independent variable, which should therefore identically vanish from the equation. This condition gives a number of equations giving relations between the constants of the equation of state.

The equations thus obtained also express relations between the constants in the expression for the law of molecular attraction, which, according to Art. 75, may be obtained from the equation of state.

82. We have seen in Arts. 76 and 77 that the constants of the law of molecular attraction may be expressed in terms of absolute constants and the critical constants  $p_c$ ,  $T_c$ ,  $v_c$ . In Art. 78 it was shown that these constants of the law may also be expressed in terms of absolute constants and the constants  $v_c$ ,  $T_c$ , and  $\Sigma c_a$  depending on the nature of the substance,

of which  $\Sigma c_a$  is the most important. At the absolute zero of temperature, when the atoms and molecules do not undergo any motion of translation, the law is likely to involve only the molecular weight and the constant  $\Sigma c_a$  depending on the nature of the substance. A remarkable confirmation of this conclusion has been obtained.

The writer has deduced\* directly from thermodynamics that the equation of state of a substance or mixture at the absolute zero of temperature has the same functional form for each substance and involves the variables  $p$  and  $\frac{v_0}{v}$  only, where  $v_0$  denotes the volume of a gram of the substance at  $T=0$  under its vapour pressure, which is zero. It was further deduced that  $mv_0$ , the molecular volume, is equal to the sum of the molecular volumes of the atomic constituents separated. This result is confirmed by the investigations of Traube†, who obtained the molecular volumes of a large number of different substances at the absolute zero of temperature by extrapolation, and showed that they are additive quantities of the atomic constituents. He also showed that

$$mv_0 = 2.6 \Sigma n \sqrt{a_w},$$

where the substance contains  $n$  atoms of atomic weight  $a_w$  relative to the hydrogen atom. The equation of state at  $T=0$  may therefore be written in a form involving  $p$  and  $\frac{\Sigma n \sqrt{a_w}}{mv}$ , where  $m$  and  $\sqrt{a_w}$  are the only quantities depending on the nature of the atoms involved. It appears, therefore, that the general equation of state given in Art. 76 may be given a form at  $T=0$  which does not involve the critical constants, but the constants  $m$  and  $\sqrt{a_w}$  instead. It will be easy to see that the law of attraction (c) under these conditions will involve only the foregoing constants which depend on the nature of the substance. The result is a confirmation of the

\* *J. Frank. Inst.* cxi. 631 (1928).

† *Phys. Zeit.* 667 (Oct. 1909).

importance of the quantity  $\sqrt{a_w}$  (or  $\sqrt{c_a}$ ) in the interaction of atoms and molecules, which has been called the attraction constant of the atom.

83. The molecular forces have an important effect\* on the total average velocity of a molecule in a liquid. We have seen in Art. 2 that when a molecule passes through a point in a substance at which the forces of the surrounding molecules neutralize each other, its velocity is the same as that which it would have in the perfectly gaseous state at the same temperature. At any other point the velocity has a different value. The total average velocity, or the average velocity of a molecule over a long distance, is in a liquid considerably larger than the velocity it would have in the perfectly gaseous state, due to the effect of molecular attraction. An expression for this velocity can be found,

Evidently no work is done on a molecule by the molecular forces in a homogeneous substance when it passes from one point to another at which the forces of the surrounding molecules neutralize each other. But its direction of motion may be changed. The pressure that the molecule exerts due to this change in direction of motion is therefore, since the velocity is the same at the two points and corresponds to the gaseous state, the same as if the molecule were in the gaseous state. The frequency of this change of motion is proportional to the total average velocity  $V_a$  of a molecule. Hence if the molecules consist of points the pressure they exert is increased in the ratio  $V_a/V$  due to the effect of the molecular forces, where  $V$  denotes the velocity of a molecule in the gaseous state. If the molecules have a volume  $b$  associated with them through which the molecules do not pass, the pressure is increased in the ratio  $v/v-b$ . The

\* *A Kinetic Theory of Gases and Liquids*, by R. D. Kleeman, chap. II. (New York: John Wiley & Sons.)

resultant pressure is equal to the expansion pressure  $P_e$  in equation (143), and we accordingly have

$$P_e = \frac{V_a}{V} \frac{RT}{m(v-b)}, \quad \dots \quad (166)$$

where  $V$  is given by the equation

$$V = \sqrt{3pv} = \sqrt{\frac{3RT}{m}}, \quad \dots \quad (167)$$

according to the Kinetic Theory of Gases, and hence

$$P_e = \frac{V_a}{(v-b)\sqrt{3}} \left( \frac{RT}{m} \right)^{\frac{1}{2}} \dots \quad (168)$$

The value of  $P_e$  may be obtained from equation (143), where  $P_n$  may be calculated according to Art. 34. Hence  $V_a$  could be calculated if the value of  $b$  were known.

84. An exact expression for  $b$  corresponding to any given temperature and density of a substance by means of which its value may be calculated and substituted in equation (168), has not yet been obtained. But approximate values of both  $b$  and  $V_a$  can be obtained by a method which will be considered in the next Article. Superior and inferior limits of  $b$  and  $V_a$  can, however, be found which are very useful. The inferior limit of  $V_a$  evidently corresponds to the superior limit of  $b$ . The latter limit corresponds to its value at the absolute zero of temperature, for since the molecules are then in equilibrium under the action of their forces of attraction and repulsion, on account of the absence of molecular motion, the molecules at  $T=0$  occupy the positions of closest approach. As the temperature is raised the distance of closest approach is evidently decreased, due to the kinetic energy of motion by the molecules. It follows, therefore, that at the absolute zero of temperature  $b=b_0$ , which is equal to  $v_0$ , the volume of a gram of substance, and is the largest value that it can have. The inferior limit of  $b$  is evidently zero.

Therefore if we write  $b=0$  in equation (168) we obtain a superior limit of  $V_a$ , and if we write  $b=v_0$  we obtain an inferior limit. Table XXXIII. gives the ratio of these limits to the corresponding velocity in the gaseous state for three liquids obtained in this way, the values of  $P_s$  being obtained from equation (143), the values of  $P_n$  from Table XIII., and the values of  $v_0$  from Art. 16. It will be seen that the values of both limits of  $V_a$  are larger than the velocity  $V$  a molecule has in the gaseous state. Since the true value of  $V_a$  lies between these limits, it follows that *the total average velocity of a molecule in a substance not obeying the gas laws is larger than that which it would have in the gaseous state.* This is an interesting and striking effect of the action of the molecular forces.

TABLE XXXIII.

	$t^{\circ}\text{C.}$	$\rho_1$	$P_n$ (atmos.).	S. L. of $V_a/V$ .	I. L. of $V_a/V$ .
Ether . . . . .	13.5	.7214	2669	11.5	3.37
Benzene . . . . .	14.4	.8840	3616	13.5	3.27
Pentane . . . . .	0	.6454	1747	5.5	2.37

It is often assumed that the average velocity of a molecule in a substance is the same as that which it has in the perfectly gaseous state. But this is entirely wrong. It holds only, we have seen, when a molecule passes through a point in a substance at which the forces of the surrounding molecules neutralize each other.

85. Approximate values of  $V_a$  and  $b$  may be obtained on writing

$$V_a = V + \frac{a_1}{v}$$

$$b = b_0 - \frac{b_1}{v},$$

in equation (168), where  $a_1$  and  $b_1$  are constants, and applying the equation to a substance at two different densities not

differing much from each other. Two simultaneous equations will be obtained from which  $a_1$  and  $b_1$  may be calculated.

86. If  $n$  denote the number of molecules crossing a  $\text{cm.}^2$  in one direction per second, and  $n_1$  the number that would cross if it behaved as a gas, it can easily be shown that

$$n = \frac{V_a}{V} n_1. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (169)$$

According to the Kinetic Theory of Gases

$$n_1 = V \frac{N_c}{4}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (170)$$

where  $N_c$  denotes the molecular concentration.

87. If the assumption is made that matter is evenly distributed in space, that is, does not consist of molecules, a number of interesting formulæ connecting some of the physical properties of matter can be deduced, which are helpful to throw further light on the properties of the molecular forces.\* We would, of course, expect that matter to a certain extent, depending on its state, would behave as if this assumption were true. This state will evidently be the more closely attained the larger the radius of the sphere of action of a molecule is in comparison with the distance of separation of the molecules, or the greater the density of the matter. The fact that the molecules of matter are in rapid motion, and that therefore each portion of space is occupied by molecules at intervals for a short time, must have the (statistical) effect of rendering the properties of matter that depend on molecular attraction more continuous in nature than they otherwise would be, and thus give rise to some of them fitting in approximately with the assumption that matter is evenly distributed in space. Assuming, then, that an even distribution of matter holds, let us find, first of all,

\* R. D. Kleeman, *Phil. Mag.* **xx**. 665 (1910).



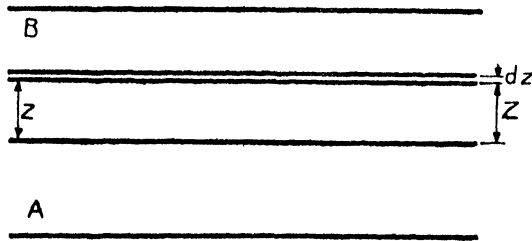
expressions for the intrinsic pressure of a substance, and the energy necessary to expand it till its volume is infinite.

Consider the attraction of a slab of matter of infinite dimensions represented by A in fig. 6 on a parallel lamina of the same material of the thickness  $dz$  situated at a distance  $z$  from the slab. The amount of matter  $\rho \cdot dz$  per square cm. of the lamina is attracted by the slab with a force which may be written

$$\{\psi(z, T) \cdot \rho\} \rho \cdot dz = \psi(z, T) \cdot \rho^2 \cdot dz,$$

since the attraction must be proportional to the square of the density  $\rho$  of the matter, where  $\psi(z, T)$  expresses the variation of the attraction between two elements of matter with their temperature  $T$  and their distance of separation  $z$ . If the

Fig. 6.



slab A were in contact with another slab of equal dimensions, the pressure per square cm. upon their surfaces of contact due to their attraction upon each other, would correspond to the intrinsic pressure of the substance. This pressure is equal to that obtained in the case of a cylinder of matter of unit cross-section, whose axis is rectilinear and of infinite length, standing with one of its bases on the slab A. The intrinsic pressure is therefore given by the equation

$$P_n = \rho^2 \int_0^\infty \psi(z, T) \cdot dz \dots \dots \dots (171)$$

Similarly, an expression for the internal work done in

distributing a gram of matter in space of infinite dimensions may be obtained. We may suppose that layers of matter of thickness  $dz$  are successively removed from the slab to infinity, and the matter in each layer then distributed in infinite space. It is evident that the thinner the layers are taken the smaller is the latter part of the work in comparison with the former. Therefore if the layers are taken infinitely thin, the former part only of the work need be considered. Therefore if a layer of matter of area  $A$  and thickness  $dz$  is removed, we have

$$U_0(A\rho.dz)=(A\rho.dz)\rho\int_0^\infty\psi(z,T).dz,$$

or

$$U_0=\rho\int_0^\infty\psi(z,T).dz, \quad . \quad . \quad . \quad . \quad . \quad . \quad (172)$$

where  $U_0$  denotes the work done per gram of matter against its attraction during the process.

A comparison of equations (172) and (171) gives

$$P_n=\rho U_0. \quad . \quad . \quad . \quad . \quad . \quad . \quad (173)$$

This equation may be applied to the facts. If  $L$  denote the internal heat of evaporation,

$$L=U_{e1}-U_{e2},$$

if there are no other internal energy changes than those connected with molecular attraction, or that  $u_1-u_2$  is small in comparison with  $U_{e1}-U_{e2}$ , where the suffixes 1 and 2 refer to the liquid and vapour states respectively. If the density of the vapour is small,  $U_{e2}$  may be neglected in comparison with  $U_{e1}$ , and equation (173) applied to a liquid under these conditions may therefore be written

$$P_n=\rho L. \quad . \quad . \quad . \quad . \quad . \quad . \quad (174)$$

Table XIII. contains the values of  $P_n$  calculated \* by means

\* R. D. Kleeman, *Proc. Camb. Phil. Soc.* xvi, (6) 545 (1912).

of this equation, and those given by the thermodynamical equation (67) in Art. 34. The two sets of values on the whole differ little from each other, showing that a liquid behaves approximately as if the matter were evenly distributed in space.

It is of interest to point out that, if matter consisted of molecules and an inverse fourth power law of molecular attraction held, equation (173) would represent the facts. Thus suppose that the attraction between two molecules separated by a distance  $z$  is given by the expression  $B/z^4$ , where  $B$  denotes a quantity depending only on the nature of the molecules and their temperature, the value of  $L$ , according to the investigation in Art. 6, would then be given by

$$L = B_1 \frac{\rho}{m^2}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (175)$$

where  $B_1$  depends only on the nature of the liquid and its temperature. Now according to equation (66) in Art. 33 we have

$$P_n = - \left( \frac{\partial L}{\partial v} \right)_T = \rho^2 \left( \frac{\partial L}{\partial \rho} \right)_T,$$

which becomes

$$P_n = B_1 \frac{\rho^3}{m^2} = \rho L.$$

The inverse fourth power law thus roughly represents the facts, as has already appeared from Art. 74.















